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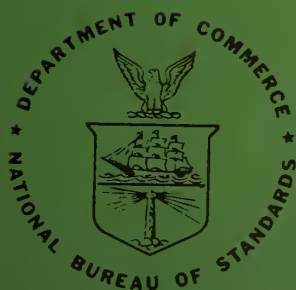
NBS

TECHNICAL NOTE

452

Spectrochemical Analysis Section:

**Summary of Activities
July 1967 to June 1968**



**U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards**

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UNITED STATES DEPARTMENT OF COMMERCE
C. R. Smith, Secretary
NATIONAL BUREAU OF STANDARDS • A. V. Astin, Director



TECHNICAL NOTE 452

ISSUED SEPTEMBER 1968

**Spectrochemical
Analysis Section:
Summary of Activities
July 1967 to June 1968**

Edited by Bourdon F. Scribner

Spectrochemical Analysis Section
Analytical Chemistry Division
Institute for Materials Research

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of nine Sections and about 100 technical personnel encompassing some 45 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the Sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is a highly important output of our laboratories. In addition, however, it has been our experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information about our programs. A word is perhaps in order about the philosophy of these yearly progress reports. In any research program a large amount of information is obtained and techniques developed which never find their way into the literature. This includes the "negative results" which are so disappointing and unspectacular but which can often save others considerable work. Of importance also are the numerous small items which are often explored in a few days and which are not important enough to warrant publication -- yet can be of great interest and use to specialists in a given area. Finally there are the experimental techniques and procedures, the designs and modifications of equipment, etc., which often require months to perfect and yet all too often must be covered in only a line or two of a journal article.

Thus our progress reports endeavor to present this information which we have struggled to obtain and which we feel might be of some help to others. Certain areas which it appears will not be treated fully in regular publications are considered in some detail here. Other results which are being written up for publication in the journal literature are covered in a much more abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1968 we plan to issue these summaries for all of our Sections. The following is the fourth annual report on progress of the Spectrochemical Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

This is the fourth in a series of annual progress reports of the Spectrochemical Analysis Section of the Analytical Chemistry Division. The Section is concerned with instrumental elemental analysis, especially for those spectroscopic techniques that are capable of multi-element determinations. These include optical, x-ray, and mass spectroscopy.

Chemical elements are uniquely identified by the characteristic frequency of emitted spectra, and amounts present can be determined by measurement of the intensity of emitted radiation. However, many factors enter into successful spectral analysis and must be carefully controlled. These include, in optical and x-ray spectrometry, the production of radiant energy by excitation, the dispersion of radiant energy into a spectrum, and the measurement of spectral wavelengths and intensities. In a similar way, spark source mass spectrometry involves ion formation, dispersion into a mass spectrum, and measurement of intensities for recorded masses. In general these are methods of comparative analysis in which calibration by synthesized or analyzed standards is required.

The research program of the Section is directed largely toward a better understanding of the phenomena involved in producing and measuring optical and x-ray emitted energy and mass spectra, and the improvement of spectrochemical methods, instruments, and calibration procedures. Included in the work of the Section are the development of appropriate standard reference materials, analyses of materials to assist other research projects, and literature surveys such as bibliographies and critical reviews.

The purpose of this report is to review the program, facilities, and accomplishments of the Section for the past year.

In order to specify procedures adequately, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

Bourdon F. Scribner, Chief
Spectrochemical Analysis Section

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ACTIVITIES OF THE NBS SPECTROCHEMICAL
ANALYSIS SECTION

July 1967 through June 1968

Edited by Bourdon F. Scribner

ABSTRACT

A summary is given of activities of the NBS Spectrochemical Analysis Section for the year July 1967 through June 1968. This covers research activities, improvement in equipment, and applications in analysis including the certification of standard reference materials. In optical spectrometry studies were completed on the plasma torch as a means of excitation of solutions, and on computer programs for the calibration of photographic emulsions. In electron probe microanalysis a matrix scanner for automatic point-by-point grid scans was tested and a lithium-drifted silicon detector was installed for non-diffractive x-ray dispersion. A study was made of color composites for combining the information of three x-ray area scans. In quantitative probe analysis, measurements were made of x-ray mass attenuation coefficients, and a study of atomic number corrections is underway. In x-ray fluorescence considerable improvement was realized by replacement of electronics by solid state circuitry, and methods are being studied for corrections of interelement effects, utilizing the digital computer. Spark source mass spectrometry was applied, by means of chemical separations and by isotope dilution techniques, to the accurate determination of impurities in zinc, platinum, and gold. A critical study was made of the uniformity of response of ion-sensitive emulsions over the area of the plates used in the mass spectrometry. Improvements in the Section's equipment and further developments in computer applications are also discussed. Listings are given of 23 publications and 19 talks by members of the Section during the year.

Key words:

Computing, digital readout, electron probe, emulsion calibration, emulsion sensitivity, gold analysis, isotope dilution method, x-ray mass attenuation coefficients, microprobe grid scanner, optical spectrometry, plasma torch, platinum analysis, preconcentration, silicon detector, spark source mass spectrometry, spectrochemical analysis, standard reference materials, time-shared computer, x-ray absorption coefficients, x-ray fluorescence analysis, zinc analysis.

1. INTRODUCTION

In the three preceding annual reports in this series we have described the program and facilities of the Section in some detail. The first report [1] described the basic program in the areas of optical and x-ray spectrometry, enrichment techniques, and standard reference materials, and also the equipment that was installed at the old NBS location. The second report [2] described the new Section laboratories at the Gaithersburg site with typical examples of laboratory facilities. A description was also given of the program and equipment of the spark source mass spectrometry group which had been added to our Section during that year. Last year's report [3] described some additions to equipment, especially digital readout devices, and outlined extensive applications of computer reduction of data. In each report, the research activities and the output in terms of publications, talks given, and analytical work have been recorded.

A. Facilities

The equipment of the Section will be briefly reviewed as background for this report. The major equipment now includes the following:

- 3-meter Eagle mounting grating spectrograph
- 3.4-meter Ebert mounting grating spectrograph
- 21-foot Wadsworth mounting grating spectrograph
- 2-meter multi-channel optical spectrometer
- 3-meter multi-channel optical spectrometer
- 1.5-meter multi-channel vacuum optical spectrometer
- 0.75-meter Ebert mounting, scanning spectrometer
- 0.75-meter Czerny-Turner mounting spectrograph/spectrometer
- Multi-channel x-ray fluorescence spectrometer
- Single-channel vacuum x-ray fluorescence spectrometer
- Electron probe microanalyzer with 3 x-ray spectrometers
- Spark source mass spectrograph

Accessory equipment includes microphotometers, sample preparation devices, microscopes, teletypewriter readout devices, etc.

Improvements in equipment this year consist largely of newly available electronic components which have been added to bring certain equipment up to high standards of stability and precision. These include a new readout system for the 3-meter optical spectrometer, an automated grid scan and a silicon detector for the microprobe, and new solid state components for the single-channel x-ray spectrometer. For observation of the spectra of weak light sources, such as laser generated vapor plumes, a 0.75-meter f/6.3 optical spectrograph-spectrometer has been obtained. This equipment is described in appropriate sections of this report.

B. Activities

The Section is organized into four major groups: optical spectrometry, x-ray spectrometry, spark source mass spectrometry, and enrichment techniques. All of the groups are engaged in research and in analysis, including the analysis of standard reference materials. The research, which constitutes about one-half of the effort of the Section, is often generated by the analytical problems encountered but may involve basic studies of considerable complexity.

In optical spectrometry major attention is directed to the study and improvement of excitation sources. In recent years the plasma jet, gas sheathed arcs and sparks, and the laser probe have been studied. This year the activity has been concerned with the plasma torch. Attention has also been given to measurement and calibration problems such as the calibration of photographic emulsions.

In x-ray spectrometry the electron probe microanalyzer has been developed to a tool with many important applications. With the improvement in electronic control and measurement devices as described in this report much tedious work with

this instrument can be automated. Quantitative electron probe analysis is being systematically investigated with the purpose of reducing the requirements for standards having compositions closely resembling the samples.

In x-ray fluorescence analysis attention is being given to the problem of correction for matrix affects, again in an effort to improve quantitative measurement and to reduce the number of standards required.

Spark source mass spectrometry provides a unique tool for survey analysis, being capable of detecting all elements in the periodic system at very low concentrations. The problem of obtaining quantitative analysis is severe and studies of the variables, such as uniformity of the ion sensitive emulsion, are being made. To by-pass many of the measurement problems the application of combined techniques of chemical separations, isotope dilution, and the spark source is proving highly effective in the determination of trace elements in standard reference materials.

The magnitude of the second major part of the activity of the Section -- analysis of materials -- is shown by the following compilation for each of the areas of analysis.

	<u>Samples</u>	<u>Determinations</u>	<u>Reports</u>
Optical emission	266	14,598	154
Microprobe	61	6,840	24
X-ray fluorescence	294	2,498	14
Spark source mass	34	1,186	13

These figures include analyses of standard reference materials which constitute about two-thirds of the samples analyzed. Examples of this activity are shown in the certificates of analysis for cast steel, ductile iron, and platinum metal given in the Appendix to this report.

In addition to research and analysis, the Section is involved in other activities of benefit to the spectroscopic field. We may include here the preparation of reviews and

bibliographies, consulting on instrumental and analytical problems, and the organization of discussion meetings on analytical problems of critical importance.

The biennial review on Emission Spectrometry was published this year; another review is forthcoming on the electron probe. Bibliographies are in preparation in both of these fields.

Two meetings held recently at NBS demonstrate a productive type of group attention to analytical problems. A meeting of a small group on quantitative microprobe analysis, held June 1967, has resulted in a 300-page book on this subject which is currently being released. The meeting was arranged by Dr. Heinrich who has edited the papers constituting the book. In October, 1967 a workshop on mass spectrometry was held at NBS with Dr. Ahearn and Dr. Paulsen as co-chairmen. It is expected that this workshop will be held periodically as the need continues.

An area of considerable interest, in which the Section has been of assistance to others, is the application of computer techniques. A description of this work with outlines of some 13 computer programs has been published in the past year [4]. This effort is continuing and programs of value to our own work are proving useful to others.

Two programs, recently developed by Mr. Rasberry of our Section, apply generally to the processing of data recorded on paper tapes. Because of the general utility of these programs, we include brief descriptions in the following section. Other computer applications are described in the body of the report.

B. F. Scribner

C. Computer Programs for Processing of Data Recorded on Paper Tape

Two FORTRAN programs, CPUNCH, and MTPRNT, and a FORTRAN subroutine, PTLOAD, have been written to facilitate the reduction of data which is stored on paper tape when a computer has no direct facility for paper tape processing. These programs are for tapes containing integer numeric data in tabular arrangement. Normally, paper tapes automatically produced as output of scientific instruments are of this type.

Descriptions of these programs and illustrations of application options are given in the following sections. One of the important techniques described here is the use of MTPRNT for one-pass processing of data recorded on paper tape by OMNITAB, the NBS general purpose statistical and numerical analysis program.

Listings of program decks, control cards, and example data are available on request to this laboratory.

1. Program PTLOAD

PTLOAD is a FORTRAN subroutine (approximately 48 statements) which loads, into the calling program, data which have been transcribed from paper tape to magnetic tape. It may be called by any program and is required by both CPUNCH and MTPRNT. As an example of the action of the subroutine, let us consider a call made as follows:

CALL PTLOAD (NUMBER, 100, 6)

This call causes characters to be read into core memory from the magnetic tape until 600 numeric characters have been found. These integers are packed into 100 six-digit numbers which are transferred to the main program as the vector NUMBER (1) through NUMBER (100).

Re-forming tables of data is left to the main program and should be arranged to account for the order (either row-order, or column-order) of the data on the original paper tape.

OFF - LINE
DIGI - DATA



2 - FOR - 1 CONVERSION

ON - LINE
UNIVAC 1108

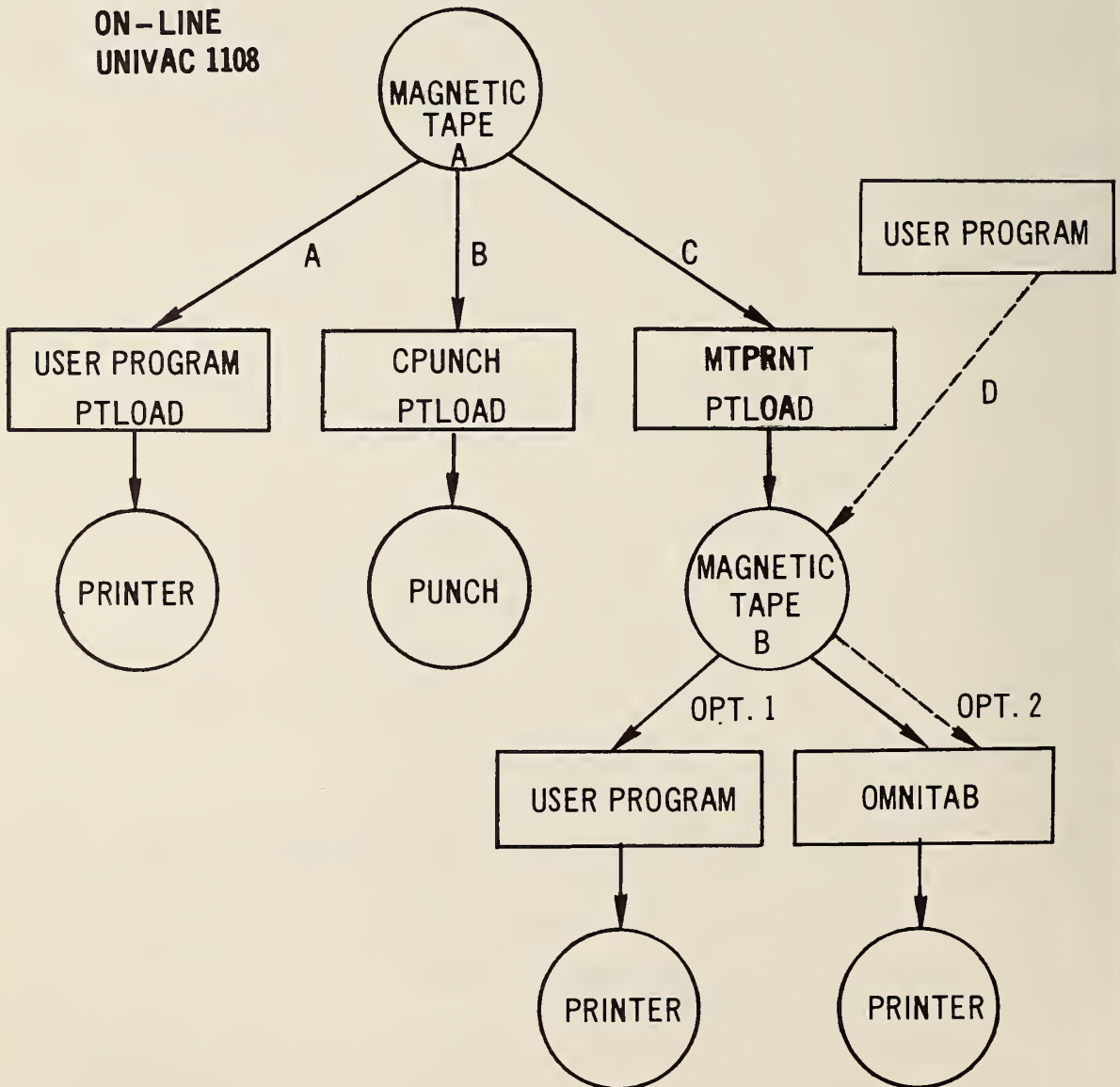


Figure 1. Flow chart for processing data recorded on paper tape.

Three uses of PTLOAD are illustrated in Figure 1. Each time PTLOAD is entered a direct listing of the vector NUMBER is printed.

2. Program CPUNCH

CPUNCH is a FORTRAN program (approximately 35 statements) which is used in the transcription of data from paper tape to punched cards. After data have been loaded into this program by PTLOAD they are ordered to the format of the original data table or to specifications provided by the user. When formation of the table is complete, those columns specified by the user for output are punched, in column order, onto cards. This program is especially useful when data editing is required. See path B of Figure 1.

3. Program MTPRNT

MTPRNT is a FORTRAN program (approximately 35 statements) which is used in the restructuring of data from an input magnetic tape with the new image written on a second magnetic tape. After data have been loaded into this program by PTLOAD, they are ordered to the format of the original data table or to specifications provided by the user. When formation of the table is complete, those columns specified by the user for output are recorded, by columns, on magnetic tape in card images.

Columns of data stored in this fashion may be processed by any appropriate program; however, one of the principal uses for MTPRNT is one-pass OMNITAB processing of data recorded on paper tape. These techniques are options 1 and 2 of path C in Figure 1. Option 2 is also useful, via path D, to extend the utility of OMNITAB to the user's FORTRAN programs.

S. D. Rasberry

2. OPTICAL SPECTROMETRY

During the past year, two research projects have been completed. One was a study of a high-frequency, induction-coupled, plasma torch; two papers describing the results of this investigation are in press [5, 6]. In addition, a thorough study has been made of the computer program KAISER for calibration of photographic emulsions.

The facilities for optical spectrometry have been improved by the installation of a new digital readout for one spectrometer and by the purchase of a high-aperture spectrograph/spectrometer, together with associated optical and electronic equipment, for use with the laser probe and other low-intensity light sources.

The vacuum spectrometer described in the last report in this series [3] has been checked out and placed into operation. However, much investigation is still needed to establish **proper** operating conditions for some of the unusual **samples** that we are called upon to analyze.

Homogeneity testing and analysis of Standard Reference Materials continue to be major efforts in optical spectrometry. The number of man-years devoted to this activity is increasing rather steadily. This is due in part to the increasing number and variety of Standard Reference Materials being prepared. The analytical problems become more complex as new types of materials are encountered or as additional elements are certified in replacement Standard Reference Materials.

A. New Equipment

1. Spectrometer Readout

Figure 2 shows a new readout that has been installed on one of the emission spectrometers. It replaces a unit which was, as far as we know, the first digital readout on any emission spectrometer. The new readout incorporates



Figure 2. Digital readout for emission spectrometer. (The large console contains the integrating capacitors and electronics for dark-current and background correction and digitizing. Data are printed on the teletypewriter).

several features which were not in the unit it replaces, and it assures improved reliability through the extensive use of solid-state electronics.

The primary data from the readout are four-digit numbers which are inversely proportional to the logarithms of the intensity ratios being measured. Up to 18 four-digit numbers of this type, together with auxiliary information, are printed on a teletypewriter and simultaneously punched into the paper tape. The auxiliary data include a serial number for each run, the sample number, and a check voltage reading that provides a test of the readout electronics on each run.

The readout incorporates several optional features. These include provisions for correction of the signal from each photodetector for dark current, and for correction of each line intensity for background. Also, optional formats for the readout are provided.

The readout format used in a particular case depends on how the data are to be handled subsequently. When a relatively small amount of data is recorded, as when the number of samples and the number of elements determined are few, the format shown in Figure 3 is used and the data may be processed on a time-sharing computer. In Figure 3 the first number on each line is the serial number for the run,

042Q DATA 4190,1797,2561,0782,3401,1653,2322,2975,1852,0605,2113

Figure 3. Readout format for data to be processed on a time-sharing computer.

which also serves as the line number for the computer. This is followed by the word DATA, as required by the time-sharing computer we use. The following data points are separated by commas, as the computer also requires. The first four-digit number after the word DATA is the sample number, which was entered by the operator on a dial switch on the readout. This is followed (optionally) by the reading for the background channel and a check voltage reading, and then by the readings for the analytical channels.

For extensive data, it is more efficient to do the calculations on the batch-loading computer in the NBS computer center. The same format shown in Figure 3 could be used for that computer, but an alternate format, shown in Figure 4, is available. In this case, the data follow the same sequence as in Figure 3, but the word DATA and the commas are omitted. When the number of analytical channels read

is too large for the data to fit on one line, the numbers continue on a second line. In the example shown in Figure 4, 18 analytical channels were recorded.

```
0421 4190 1797 2561 0782 3401 1653 2322 2975 1852 0605 2113 2022
1772 1615 0802 2386 2590 3213 0345 3090 2555
```

Figure 4. Readout format for data to be processed in the NBS computer center.

The large NBS computer does not presently provide for direct data input via the punched paper tape from this readout. Therefore, when the data are to be entered into that computer, they are first transferred to a magnetic tape, as is described in Section 1C of this report.

Another digital readout, described in the last report [3, p. 9] has been modified slightly to improve its performance. Previously, the signal was digitized during a one-second period after stepping to each capacitor in the spectrometer console. A one-half second delay has been interspersed between the stepping signal and the start of digitizing to permit the electrometer amplifier which couples the capacitor to the digitizer to come to balance. A second modification provides a warning when the charge on any capacitor exceeds 10 volts. In that case, the characters "XXXX" are printed in place of the four-digit number normally given.

Until recently, the computer processing of data from the spectrometers had been restricted primarily to the statistical computations required in homogeneity testing. A program for fitting analytical curves, described in the last annual report [3], has been tested extensively and appears to give good results. This program is now being used on the time-sharing computer to process analytical data, and it is being translated into FORTRAN for the large computer in the

NBS computer center. We anticipate that in the near future it will be possible to have analytical results for as much as a whole day's work on the spectrometer processed in a few minutes.

2. High-aperture Spectrograph

Figure 5 shows the high-aperture spectrograph which has been purchased for use with the laser probe and other low-intensity sources. It is a Czerny-Turner mount, grating spectrograph with a focal length of 0.75 m. With a grating approximately 100 mm square, the optical aperture is about $f/6.3$, depending on the grating angle. As a spectrograph, the instrument can accommodate 4 x 10 in. plates or Polaroid film; as a photoelectric spectrometer, one exit slit is now installed and an attachment can be added later to provide more exit slits if they are needed.

Experience with a large $f/30$ spectrograph and a few exposures on an $f/1.5$ instrument indicated that an aperture between $f/5$ and $f/10$ would be approximately optimum for the laser probe when pit sizes are about 50 μm in diameter. An instrument with a larger aperture might permit working with considerably smaller samples, but it would require the acceptance of much poorer resolution and dispersion at the present state of spectrograph design: Nevertheless, the new instrument should make it possible to obtain good spectra with considerably smaller samples than we have been able to analyze previously with the laser probe. Alternatively, for quantitative analysis, it will be possible to employ emulsions providing improved photometric precision at the expense of poorer sensitivity.

The new spectrograph is equipped with a 1200 groove/mm grating, giving a reciprocal linear dispersion of about $10 \frac{\text{\AA}}{\text{mm}}$ in the first order. The photographic resolution is 0.2 \AA or less over several hundred angstroms, and the resolution is about 0.1 \AA at the exit slit for photoelectric

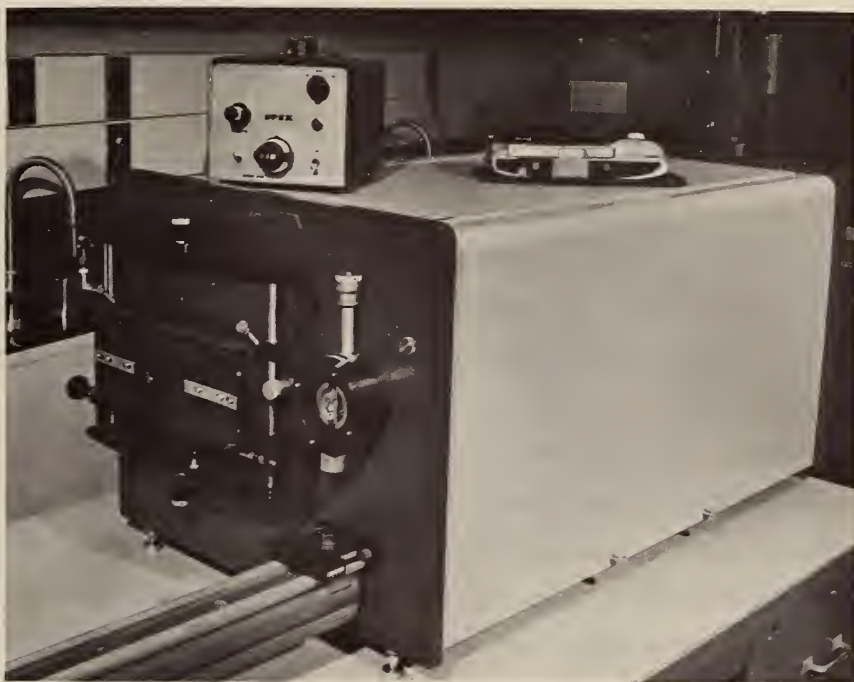


Figure 5. High-aperture spectrograph for use with low-intensity light sources.

measurements. It is expected that this resolution will be adequate for the relatively weak spectra obtained with the laser probe.

When any spectrograph is used with a weak light source, it is essential that the illuminating system transmit light as efficiently as possible. For use with this spectrograph, a Cassegrain illuminator is on order, which is designed to provide considerably better illumination than would be possible with a simple lens system. This illuminator will have two modes of operation. For qualitative analysis, the illuminator will form an image of the source on the entrance slit of the spectrograph with a magnification near unity. For quantitative analysis, the illuminator will form an enlarged image, several centimeters in front of the entrance slit, which will serve as a virtual source; the image may be

diaphragmed at this point if it is desired to select light from a portion of the discharge. An achromatic lens will form an enlarged image of the virtual source on the collimator, and the system is designed to give evenly-exposed line images over several millimeters of the height of the slit, permitting the use of a step filter.

The electronics to go with this instrument are designed to be used with stable light sources, such as flames and hollow-cathode lamps, and with pulsed sources, such as the laser probe. For stable sources, the electronics include a regulated high-voltage power supply, a phase-sensitive amplifier, and a strip-chart recorder. Electronics for pulsed sources will include an amplifier providing for display of intensity vs. time on an oscilloscope, with a time resolution of about 1 μ sec, or, alternatively, displaying on a meter the intensity integrated over the duration of the light flash.

The instrumentation described here is now being installed. By the time of the next report in this series, we hope to have information on the performance of the equipment.

B. Study of Plasma Torch

In the last report [3], we described some preliminary results of a study of the properties of an inductively-coupled, radio-frequency, plasma torch. The study of this source has now been completed, and two publications on this work [5, 6] should appear shortly.

The detection limits found with this torch were encouraging, particularly the limits in emission for some of the elements which are difficult to excite in the flame. For example, the limit of detection in emission (defined as the concentration in solution at which the signal-to-noise ratio equals two) was between 0.4 and 1 μ g/ml for aluminum,

boron, molybdenum, and titanium, as well as for some elements easily determined in flames, such as silver and calcium. However, the detection limits by atomic absorption were considerably poorer in most cases, largely due to the high background emission by the torch. Hollow-cathode lamps were employed as the primary sources for the atomic absorption measurements, and it is possible that lower limits of detection would be possible with brighter primary light sources, such as electrodeless lamps.

Marked interelement effects were found with the plasma source, affecting particularly the emission signals. With one exception, the effects observed were enhancements. Table 1 lists some of the enhancement factors found, defined as the ratio of the emission or absorption signals in the presence of the interfering element to the signals in the absence of the interfering element. The Ca II line could not be measured in absorption because of the low intensity of this line from the hollow cathode lamp, and absorption measurements with aluminum were obscured by noise.

Table 1. Enhancement factors in emission and absorption

Element, at 100 $\mu\text{g/ml}$	Wavelength, $\overset{\circ}{\text{A}}$	Added species, at 100 $\mu\text{g/ml}$	Enhancement factor	
			Emission	Absorption
Ca I	4227	PO_4^{3-}	1.6	1.3
Ca I	4227	Na^+	2.7	1.0
Ca II	3968	PO_4^{3-}	7.5	
Ag I	3281	Cu^{2+}	1.3	1.0
Cu I	3248	Ag^+	1.2	1.0
Al I	3093	Ca^{2+}	0.7	

These observations were interpreted as indicating a lack of local thermal equilibrium in the discharge. If the interelement effects were due to changes in element populations, they should affect emission and absorption signals equally. Thus, chemical effects can apparently be ruled out. If there is not local thermal equilibrium, and if most excitation occurs through electron-atom and electron-ion collisions, the emission signals should increase when the electron concentration is raised by adding an additional element to the sample. This interpretation explains all of the enhancements observed, but cannot account for the suppression of aluminum emission by calcium. It is, however, possible that some chemical interferences do occur in the plasma torch and that these are counterbalanced in most cases by the enhancement effect.

Figures 6 and 7 show how the Ca I line at $4227\overset{\circ}{\text{\AA}}$ changes in intensity with increasing amounts of phosphate and aluminum added. There is relatively little additional enhancement by phosphate at concentrations above about 100 $\mu\text{g/ml}$. In the case of phosphate, it would apparently be possible to buffer the interference by adding phosphate to all samples, but this approach would not work in the case of the influence of aluminum on calcium emission.

Although the absorption signals are relatively free from the interelement effects, the detection limits were not as good as in emission.

The study was ended when it was concluded that the good emission sensitivities observed with the plasma torch do not provide sufficient advantage to counterbalance the severe interelement effects and the extra cost and difficulty of operating a plasma torch as compared to a chemical flame. For those elements which do not provide adequate emission signals in flames, the plasma jet [7] appears to be a more convenient light source than the plasma torch.

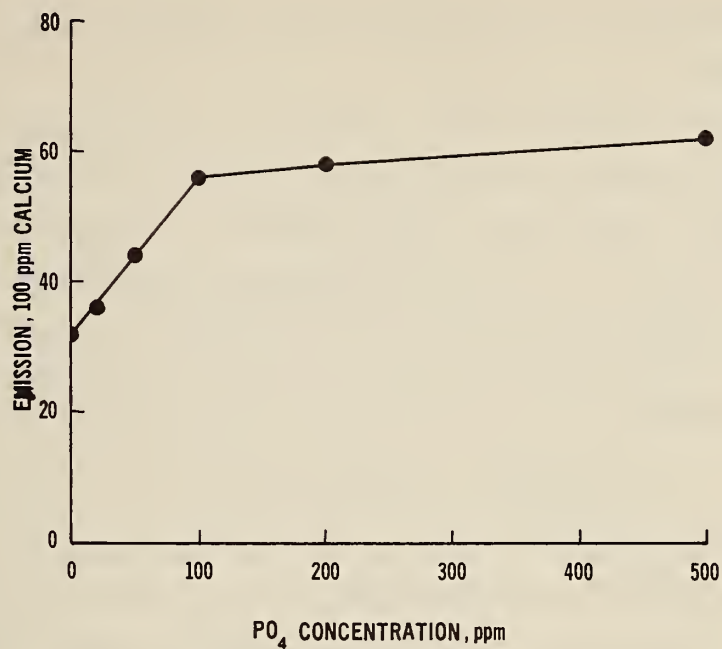


Figure 6. Effect of phosphate on calcium line emission in the plasma torch.

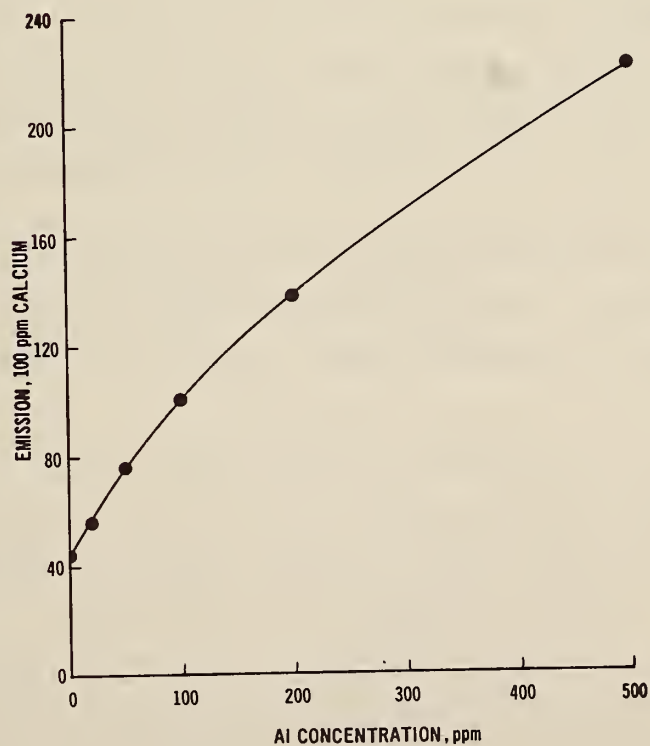


Figure 7. Effect of aluminum on calcium line emission in the plasma torch.

C. Test of Program for Calibration of Photographic Emulsions

The annual report of this Section for 1965-1966 [2, p.10] included a description of a computer program for calibration of photographic emulsions. The program is based on the concept that a function of the transmittance readings could be found for which a plot of the logarithm of the relative exposure vs the function of the transmittance would be linear and could be represented by the equation

$$\log(E_R) = M \cdot f(T) + c, \quad (1)$$

where E_R is the relative exposure, M is the slope of the line, $f(T)$ is the linearizing transform of the transmittance, T , and c is the intercept. Since only relative exposures are being determined, c can be assigned any convenient value and only the slope, M , need be determined. In principle, M could be found from the transmittance values for one pair of readings of lines of known relative exposure, such as a pair of readings through a step sector, but in practice the value of M should be determined by averaging slopes obtained from several line pairs, thus reducing the influence of random errors.

Several transforms were tested for their ability to give a fit to eq 1, and the Kaiser transform [8] was selected for a more detailed study. This transform has the form

$$K = A \log(1/T) + (1-A) \log(1/T-1), \quad (2)$$

where T is the transmittance. The constant A may be estimated from an equation given by Kaiser [8], but photometric errors make a single estimate of A unreliable.

The program KAISER calculates up to 100 values of A , determines the mean and standard deviation, and compares each value of A with the mean. Any value of A differing from the mean by more than three times the standard deviation

is rejected, and a new average and standard deviation is found. Then, for each pair of readings through a step sector or filter, a value of M is found. The average M and the standard deviation are found, and again a test is made to reject any value of M differing from the mean by more than three times the standard deviation.

The test of the method is to determine whether, under normal measurement conditions, the Kaiser transform gives an acceptable fit to eq 1. The fit is not acceptable if the values of M show a perceptible trend with increasing blackening of the lines on the plate. The measurement conditions that can affect the fit include the type of emulsion, the wavelength at which the calibration is made, the spectrograph, and the microphotometer, including possible influences of scattered light or other optical defects in the microphotometer. We have made tests of the program with five emulsions exposed on two spectrographs and measured on three microphotometers; in the case of one microphotometer, measurements were made with four slit widths, ranging from about one-tenth to one-half of the width of the entrance slit of the spectrograph. The data were inspected by plotting M as a function of the percent transmittance of the light line of the pair used to determine each value of M .

Figure 8 shows a plot of this type for an SA-1 plate exposed at 3200 Å. It is seen that there is no perceptible trend of the slope with increasing blackening of the line, indicating that the emulsion can be calibrated by means of the two parameters, A and M . Similar results were obtained with this emulsion over its entire useful wavelength range, as well as with type 33, 103-0, and II-F plates. On the other hand, Figure 9 shows the results obtained with a Q-2 plate at 3200 Å. It is clear that, for this emulsion at this wavelength, the fit to eq 1 is not satisfactory. However, at 2400 Å, a good fit to eq 1 is obtained, indicating that the calibration method can be used with Q-2 plates

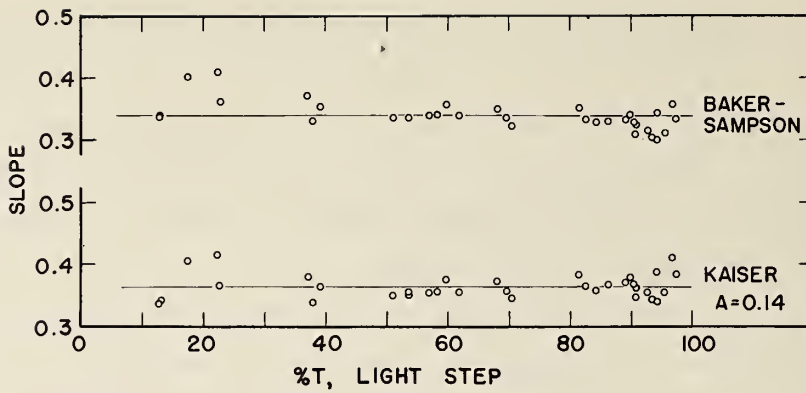


Figure 8. Computed slope as a function of relative intensity of line pair. Data for an SA-1 plate at 3200 Å.

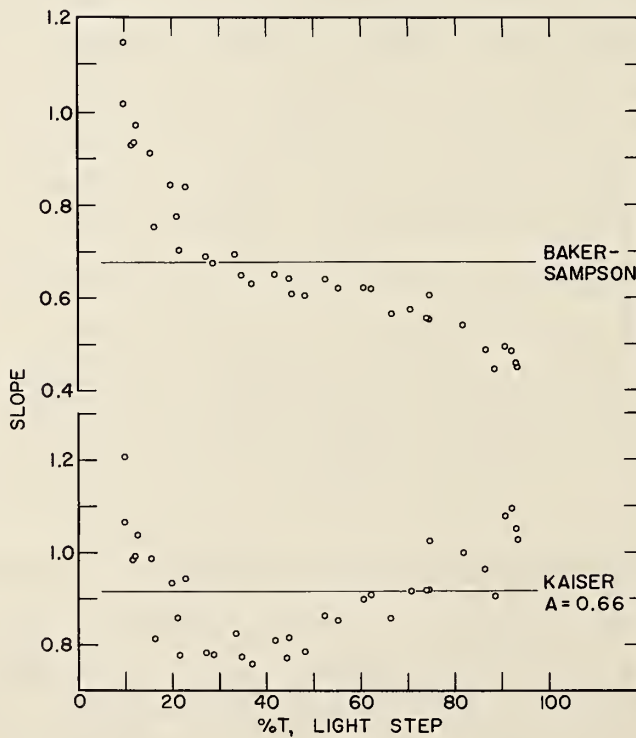


Figure 9. Computed slope as a function of relative intensity of line pair for Q-2 plate at 3200 Å.

at the short wavelengths where these plates are normally advantageous.

The effect of scattered light in the microphotometer is illustrated in Figure 10, which is a plot of data for an SA-1 plate measured in another laboratory. The microphotometer had approximately 0.5% scattered light. As a result, readings below about 10% T are affected by enough to give erroneous values for M. In this case, the emulsion calibration method is applicable only for lines having transmittance values above about 10%. The program includes provision for restricting the range of transmittance values for which the calibration is made, as is needed in an individual case.

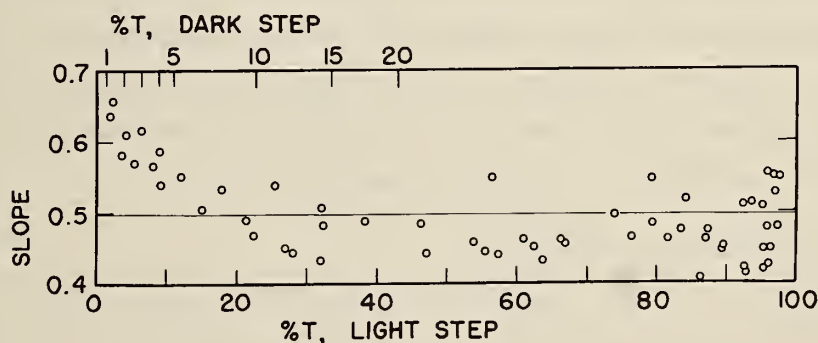


Figure 10. Effect of scattered light in microphotometer on linearity of plate calibration with Kaiser transform.

These studies have demonstrated that the method of plate calibration developed here is applicable for most emulsions under the measurement conditions we employ. The method is well adapted to a digital computer. In addition, the output of the program provides information to indicate why the method fails, if it does. Data such as are shown in Figure 10 provide evidence for scattered light in the microphotometer. A plot similar to Figure 9 will be obtained if the microphotometer is not in focus; thus, if such data are obtained for an emulsion for which earlier measurements had

indicated a good fit to eq 1, attention is drawn to the cause and steps may be taken to correct the cause of the error.

The use of a time-shared computer for emulsion calibration and conversion of transmittance readings to relative intensities has been found to save considerable time. For example, in a recent series of analyses, measurements were made for line and background transmittance values for 15 lines and the emulsion was calibrated in 5 wavelength regions. There were 10 exposures on each plate, so that measurements on the microphotometer included 150 readings of line transmittance, 150 readings of background transmittance, plus calibration data for 5 wavelength regions. Typically, calibration of the emulsion and conversion of readings to 150 relative intensities, corrected for background and step, required about one-half hour, considerably less than would be needed by graphical methods.

D. Applications to Analysis

In addition to the research activities described in this report, the facilities of the Spectrochemical Analysis Section are employed for a considerable number of other analytical applications. For the period June 1967 through May 1968 analyses were performed by emission spectroscopy involving 266 samples, 14,598 determinations, and 154 reports.

1. Standard Reference Materials

A continuing important role of the Section is in the testing for acceptance and analyses for certification of Standard Reference Materials. Nearly all of the materials, including those not directly applicable as spectrochemical standards, are subjected to general qualitative or semi-qualitative analysis. This procedure verifies the aim composition of a given material as well as indicating unexpected elements introduced in the manufacturing process.

Typical samples analyzed in the past year were metallo-organic compounds, botanical material, steels, irons, high-purity zinc, glasses, and various ferrous alloys.

Following this general type of analysis, the intended Standard Reference Materials are tested for homogeneity. Every effort is made to secure samples of these materials which can be analyzed directly on the photoelectric emission or x-ray fluorescence spectrometers. For example, samples from steels or irons intended as chemical SRM's are selected prior to the chipping process. A typical steel as received from the producer would generally be in the form of bars 8 in. in diameter by 30 in. long with up to fifteen bars per heat. Slices from both ends of each bar are obtained, and analyses are made on these slices to determine the homogeneity of the individual bars and of the entire heat. Subsequent chipping and blending of the material is made on those bars which are shown to be acceptable, to provide for the chemical Standard Reference Material.

Materials intended as standards for spectrochemical analysis are usually provided in either ingot form or chill cast slab form. Ingots up to one ton are sampled at selected points and tested for homogeneity prior to rolling to finished size. Preparation and testing of the chill cast standards have been described elsewhere [9]. Homogeneity data are usually generated on either the emission or x-ray fluorescence spectrometer, and the digitized readout provided is applicable for direct input to computers. Depending on the volume of data and speed required, the central computer facilities at NBS or the time-sharing computer is used. Applications of the time-sharing computer have been described in previous progress reports [2,3]. Spectrochemical Standard Reference Materials tested for homogeneity this past year include Cast Steels, Ductile Iron, High Temperature Alloys, Tin-lead Solders, Stainless Steel, and Electronic Nickel Alloys.

In addition to homogeneity testing, we also participate in the quantitative analyses required for certification of Standard Reference Materials. Analyses by at least two independent methods within our Section along with other analyses made at NBS and by cooperators in industry provide for the provisional and final certification.

An illustration of the overall planning, cooperative homogeneity testing, and analysis for certification is given for two cast steel Standard Reference Materials. At the request of the Steel Founders Society of America, two compositions of cast steel were prepared and cast at the American Cast Iron Pipe Co., Birmingham, Ala. with use of the NBS chill cast mold assembly. Homogeneity testing was performed by our Section, the Research Laboratories of General Motors Corp., and ten member foundries of the Steel Founders Society, and the material was found to be satisfactory. Subsequent analyses for chemical certification were made by our Section, other groups at NBS, and five member foundries of the Steel Founders Society. As a result, two new Standard Reference Materials useful for spectrochemical analysis of cast steel are being issued. A similar program for ductile iron has provided three needed standards for this material. Copies of the provisional certificates for these standards are included in the Appendix to this report.

2. Other Analyses

The Analytical Chemistry Division performs numerous analyses for other groups at NBS and for other government agencies. Whenever possible, this work is done in the Spectrochemical Analysis Section in order to take advantage of the speed and efficiency of routine spectrochemical analysis. This work ranges from qualitative to quantitative analyses depending on the nature of the sample and the specific requirements.

A typical application of quantitative analyses would be the specification testing of failed aircraft parts. Three parts of an aircraft landing structure were submitted for analyses with the information that two of the parts were good and one had failed. Spectrochemical analyses revealed that the good parts were medium alloy steel and within specification, while the failed part was plain carbon steel.

Another application involved the analyses of tin liners in copper pipe used in a distilled water system at NBS. The specifications required that the impurity content of the tin could not exceed 0.10%. Several lots of the fabricated pipe supplied by the contractor were rejected, on the basis of the spectrochemical analysis, before acceptable material was finally installed.

Qualitative and semi-quantitative analyses of corrosion products, dust, powders, liquids, and other miscellaneous samples are often performed. Semi-quantitative analysis by the gallium oxide powder dc-arc technique of metallic impurities imbedded in plastic bottles revealed the source of contamination of liquids stored within the bottles. A qualitative analysis of dust fallout showed that the dust in our own laboratories originated largely from a slotted steel beam and insulating material in the ceilings.

Many other similar applications of analyses, too numerous to mention here, were made during the past year, principally through the able work of Mrs. V. C. Stewart, Mrs. M. M. Darr, and Mr. D. M. Bouchette.

M. Margoshes, J. L. Weber, Jr.

3. ELECTRON PROBE MICROANALYSIS

A. Basic Considerations

This year's activities were intended to provide a balance among theory, technique of measurement, and applications. In the area of theory, we investigated the sources of error in quantitative procedures in order to establish priorities for subjects of further research. Technique and instrumentation were improved mainly in three areas: (1) the use of a matrix scanning device [3] for homogeneity studies and other objectives, (2) non-diffractive analysis by means of a lithium-drifted silicon detector, and (3) combining several x-ray (or electron) area scans in a color composite for better representation of spatial relations. The studies of x-ray mass attenuation coefficients were continued, and the construction of the alloy quenching device [3] was completed. Studies of applications include the investigation of homogeneity of standards for microanalysis, and the preparation and analysis of biological specimens.

B. Techniques and Instrumentation

1. Matrix Scanner

The interfacing system for automatic grid scans [3, p.34] (henceforth called matrix scanner) was installed (Figure 11) and fully tested. The system is composed of the following parts:

a. Timer-scalers. There are six of these convertible to either time or scaler.

b. Matrix-generator. This device generates a one or two dimensional matrix of variable dimensions, with a maximum size of 100 x 100 positions. This device advances one position in one dimension (the line) after completion of an x-ray signal counting interval. After the line is completed, the device advances to the first position of the next

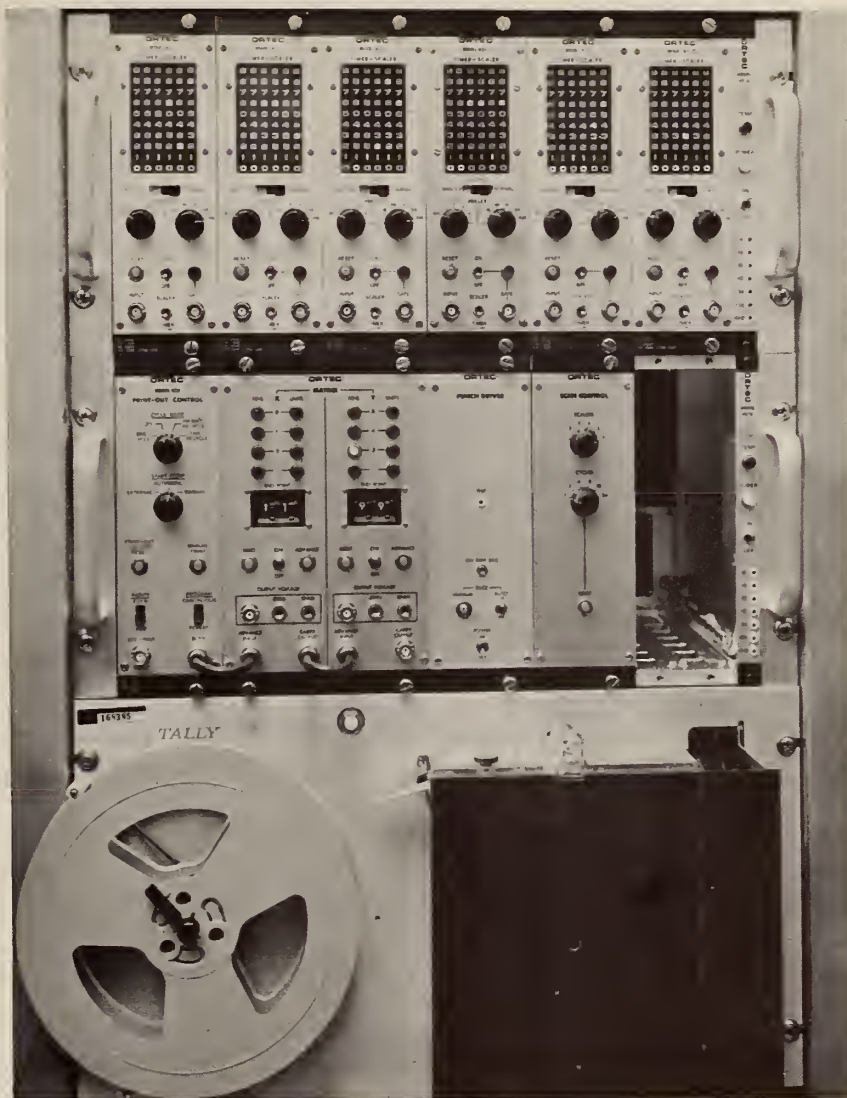


Figure 11. Device for digital matrix scanning.

line. D-c outputs proportional to the number of line and the position along the line are provided. By connecting these voltages to the electron beam scanner, the electron beam can be moved on the specimen surface forming a raster that images the matrix. The distances between positions can be varied over a very wide range.

c. Scan Control. This determines how many scaler-timers are to be read, and how many times the matrix scan is to be repeated in an automatic scan.

d. Print-Out Control. This determines if the advance and print-out of the timer-scalers is automatic or manual, and permits two forms of print-out.

e. Paper Punch. This permits fast punching of the results into paper tape, in ASCII code. The tapes thus generated can be printed by teletypewriter (Figure 12), or directly processed by a computer.

APRIL 11, SCAN 4

BIOLOGICAL STANDARD EMB 31

FE	S	NA	TARGET CURRENT	TIME	TALLY
000002	000002	000006	000001	000200	000001
000507	000228	000135	028496	000200	000002
000545	000215	000167	029935	000200	000003
000561	000244	000119	029870	000200	000004
000577	000249	000115	029826	000200	000005
000583	000235	000121	029787	000200	000006
000600	000253	000136	029750	000200	000007

Figure 12. Example of matrix scanner print-out.

The timer-scalers register time, pulse information from x-ray channels, (diffractive or non-diffractive), or digitized currents (target or monitor current). They can also be used as talliers, counting the position of a read-out within the matrix, or for sampling. In this last mode, a short counting period (e.g. 20 sec) is repeated after long periods (e.g. every 400 sec).

In a typical operation, the matrix positions correspond to positions upon the specimen. A one-dimensional matrix is used for a line scan, and a two-dimensional matrix for an area scan. The length of a counting period can be constant (fixed time mode), or it can be determined by a signal level in a scaler; hence, ratios of x-ray counts can also be registered.

Instead of using the matrix output to shift the electron beam, the device can also be used to register signal variations as a function of time, or of any variable connected with time. For instance, fixed-time periods of counting can be used, and the results punched onto tape, while the wavelength position of one or more spectrometers is advanced slowly.

This device can be used advantageously whenever a great number of measurements must be made. In our laboratory, it was employed for the analysis of diffusion couples, inclusions in alloys, and biological specimens. The main area of application is in the determination of homogeneity of alloys used as standard reference materials. A comprehensive computer program, which provides for drift compensation and gives topographic information (Figure 13), as well as statistical evaluation is presently being tested. Mr. S. Rasberry has provided great assistance on the computation problems encountered in the course of our work.

2. Lithium-drifted Silicon Detector

As mentioned in previous reports [2, p. 60; 3, p. 31], non-diffractive (non-dispersive) spectrometry by pulse-height analysis offers the advantages of (1) a very quick, although low-resolution, spectral scan, and (2) of the absence of defocusing when the electron beam is deflected from its central position. The advantages of a flow-proportional counter in the soft region (5-50 Å) were illustrated in last year's report. A solid-state silicon detector, installed during the

ABSOLUTE TOPOGRAPH

ELEMENT 1= AG LA

ELEMENT 2= AU LA

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.O 0 :  -  -  +  +  +.
.G 0 0 , : -  -  +  +  +.
.G 0 : :  :  +  +  +.
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KEY

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G	0	:	.	BLANK	-	+	*	M

Figure 13. Section of computer output for homogeneity testing.

current fiscal year, complements the flow-proportional counter. The useful wavelength range of the silicon detector (the photon energy must be above 1 keV) overlaps that of the proportional counter. The resolution of the silicon detector (in the order of 600 keV half-width) is far superior to that of the gas detectors (except for the low energy extreme of the observable range); the pulse-height is very stable, and high counting rates (up to 5×10^4 counts/sec) can be observed. A moderate disadvantage of this detector is the need for constant cooling to liquid nitrogen temperature (Figure 14).

Since defocusing effects and count-rate limitations limit the usefulness of the matrix scanner, it is expected that combination of the latter with the silicon detector will

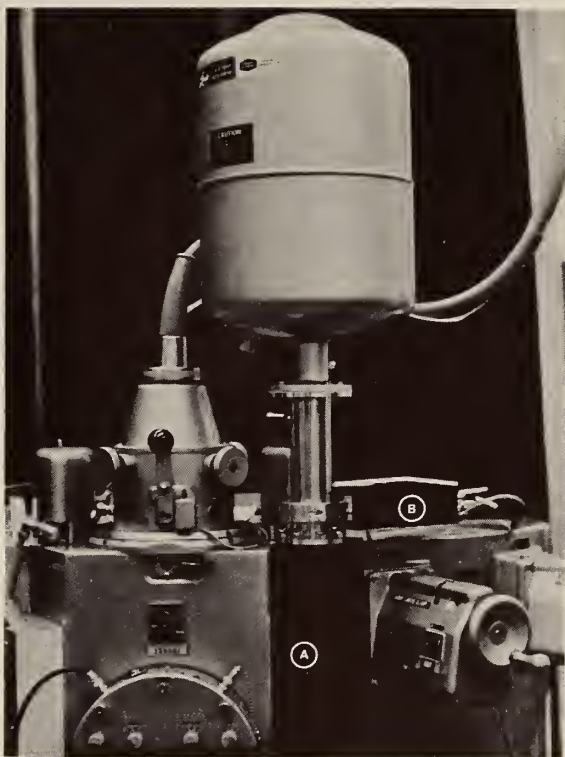


Figure 14. Non-diffractive silicon detector mounted on electron probe micro-analyzer. (A) solid state detector, and (B) preamplifier.

be particularly useful. Examples of spectra obtained with the detector are shown in Figures 15 and 16. A more complete study of the detector is presently under way.

3. Color Composites for Area Scanning

Color photography has been used in several instances to combine x-ray area scans of several elements in one image. This simplifies the interpretation of area scans, since the topographic interrelations of concentrations of the elements involved appear more clearly.

This technique was studied in detail, in cooperation with H. Yakowitz (Metallurgy Division), in order to compare various techniques of color registration, and to establish working rules for applying color mixing to x-ray area scans.

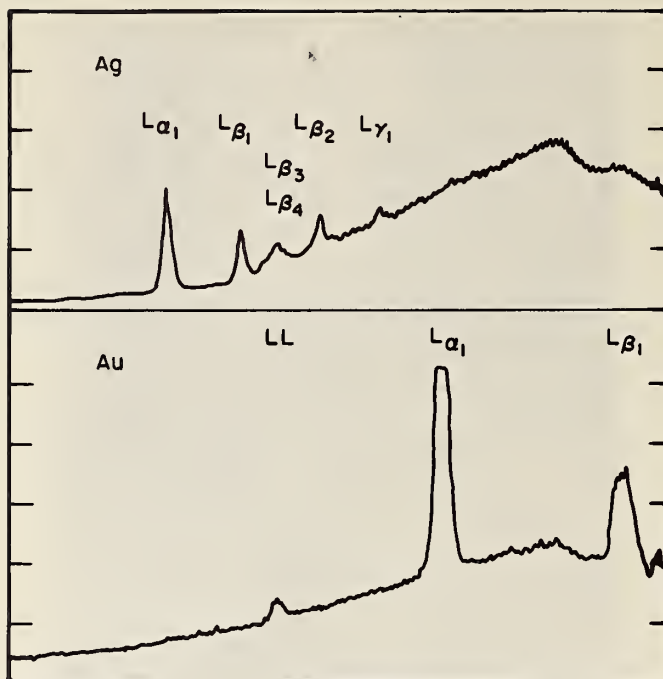


Figure 15. Diffractive spectra of a 60 gold - 40 silver alloy. (Upper spectrum, ADP crystal; lower spectrum, LiF crystal).

It was found that color composites combining the information for up to three x-ray area scans can be prepared most efficiently by copying on color film the partial black-and-white exposures, and using a different color filter for each exposure. A simple jig can be used to achieve satisfactory superposition of the partial images. The technique and several applications will be published [10].

C. Quantitative Electron Probe Microanalysis

1. X-ray Mass Attenuation Coefficients

Experimental measurements of the mass attenuation coefficients of 15 elements were performed in the region from 0.5 to 8.3 Å, using a modified x-ray fluorescence spectrograph. The measurements were performed on foils. The characteristic lines were obtained by inserting, in the specimen position of the spectrograph, pure elements or in some cases

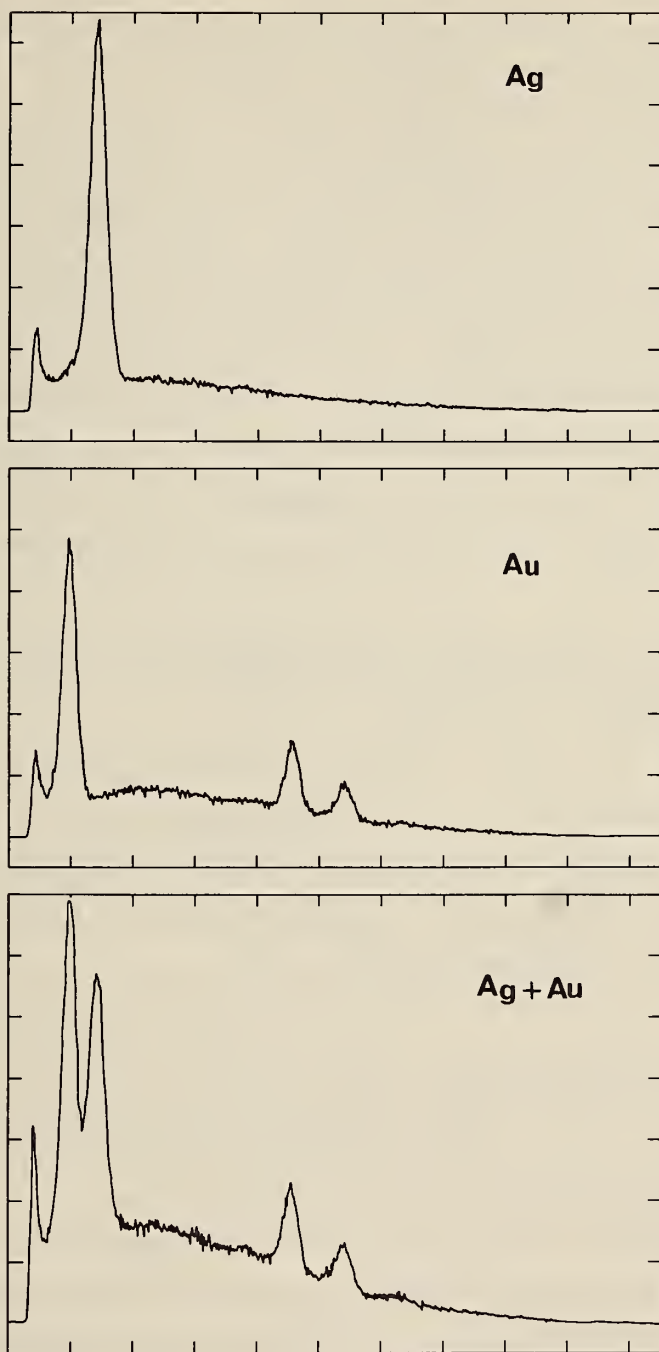


Figure 16. Non-diffractive spectra of Ag, Au, and a 60 Au - 40 Ag alloy.

simple compounds. The absorbers were inserted between the first collimator and the analyzing crystal.

In most regions the values obtained check with the observations of previous investigators, as well as with our previous interpolations [11] within 2-4%. Hence, in these regions we can consider the mass absorption coefficients sufficiently well known for the purposes of quantitative electron probe microanalysis. However, towards longer wavelengths, discrepancies among published values increase, and the accuracy of measurements is limited by the availability of thin foils. Studies of preparation of thin foils are presently under way. This work was ably performed by Dr. P. K. Hon.

2. Study of Uncertainty in Corrections for Quantitative Analysis

The results of these studies of the absorption and fluorescence corrections are now published [12, 13]. Similar studies were extended to the atomic number correction; we expect to publish the results during next fiscal year. The main conclusions of these studies are:

1. In order to minimize serious errors due to the absorption correction, it is advisable to work at relatively low energies, and with high x-ray emergence angles. There is no serious objection to this from the point of view of the atomic number or fluorescence corrections.

2. Since the so-called atomic number correction is affected by the atomic number-to-atomic mass ratio, this correction is frequently not negligible for elements not too far apart in the periodic table. The uncertainty in the values of the mean excitation energy for low atomic number elements causes serious uncertainties in the analysis of oxides, carbides, and similar compounds, even when the heavier element is determined.

3. Although the uncertainties discussed above may be reduced by careful analysis of well-characterized standards, their effects, in conjunction with the absorption correction uncertainties and the chemical effects on x-ray emission seem to preclude the possibility of accurate quantitative determination of elements of atomic number below 10, unless standards closely matching the specimen are available.

3. Standard Reference Material Measurements

An extensive search for well-characterized materials which would be of use in testing the theory of quantitative analysis resulted in the gathering of several dozens of materials of unquestionable usefulness. Careful measurements over a wide range of experimental conditions will be performed within the next fiscal year, and they will be published together with complete documentation of the characterization. Some of these materials (including a series of copper-gold alloys and one of silver-gold alloys) will be available as certified standard reference materials. Some others will be available on loan to requesters. The results of these measurements will be used to test the efficiency of current procedures for data reduction.

4. Proceedings of a Seminar on Quantitative Electron Probe Microanalysis

On the occasion of the Seminar on quantitative electron probe microanalysis mentioned in the 1967 report [3], a series of papers concerning diverse aspects of quantitative microprobe analysis were obtained from various participants. These papers have been issued in hard-cover book form under the title: "Quantitative Electron Probe Microanalysis", NBS Special Publication 298, August 1968. The volume contains the following contributions:

Introduction

L. S. Birks, Naval Research Laboratory, Washington, D. C.

Quantitative Electron Probe Microanalysis. A Progress Report

K. F. J. Heinrich, NBS, Washington, D. C.

Some Problems with Quantitative Electron Probe Microanalysis

J. Philibert and R. Tixier, Research Institute of the French Ferrous Metallurgy (IRSID), St. Germain-en-Laye, France.

The Theory of Quantitative Electron Probe Microanalysis

I. B. Borovskii, and V. I. Rydnik, Institute of Metallurgy, USSR Academy of Sciences, Moscow.

On the Structure of Formulas for Quantitative Analysis

J. Criss, Naval Research Laboratory, Washington, D. C.

Computational Methods for X-ray Emission from Targets Excited by Electrons

D. B. Brown, University of Southern California, Los Angeles, California. (Now with Naval Research Lab.)

The Choice of Models for Electron Scattering and Deceleration for Electron Probe Microanalysis

T. Mulvey, University of Aston in Birmingham, England.

Progress in the Correction for the Atomic Number Effect

D. M. Poole, Atomic Energy Research Establishment, Harwell, Didcot, Berkshire, England.

The Calculation of Stopping Power and Backscatter Effects in Electron Probe Microanalysis

P. Duncumb, Tube Investments Research Laboratories, Saffron Walden, England, and S. J. B. Reed, Mineralogy Department, British Museum, London.

Scattering of Electrons in Metallic Targets

K. Murata, R. Shimizu, and G. Shinoda, Osaka University, Higashinoda, Miyakojima, Osaka, Japan.

Absorption Edge Effects in Electron Probe Analysis

D. Nagel and J. Criss, Naval Research Laboratory,
Washington, D. C.

Fluorescence Excited by the Continuum

J. Hénoc, National Center for Studies of Telecommunica-
tion, Moulineaux, France.

Quantitative Evaluation Methods for Alloy Microstructures
by Microprobe Analysis

G. Dörfler, Analytical Institute, University of Vienna,
Austria.

Some Aspects of the Microprobe Analysis of Biological
Specimens

T. Hall, Cavendish Laboratory, Cambridge, England.

5. Literature Research

Work on the bibliography has continued but was slowed
down by changes in personnel and by the work connected with
the Seminar described above.

K. F. J. Heinrich

4. X-RAY FLUORESCENCE SPECTROMETRY

Improvements in instrumentation, methods, and computing software have made possible more precise and accurate measurements, benefitting our research program as well as the NBS Standard Reference Materials (SRM) programs. Research into improved methods of calibration and correction techniques for interelement interferences has continued and will soon be applied to the analysis of high-temperature alloys and nickel-base electronic alloys.

Much of the x-ray fluorescence project has been directed toward the analysis of chemical compositions and the determination of plating thickness for certification of SRM's. Support to the Office of Standard Reference Materials has been provided through homogeneity testing, specimen sorting, and rapid verification of composition of labeled specimens.

A. Modification of Equipment

The Spectrochemical Analysis Section is equipped with a single-channel x-ray fluorescence spectrometer (the Norelco Four Specimen Vacuum Spectrometer) and a multi-channel x-ray fluorescence spectrometer (the Applied Research Laboratories, Inc., PXQ). These instruments were described earlier [1, pp. 30-34].

The single-channel instrument is of modular design and has been improved by replacement of the entire signal processing and counting electronics. The first phase of this change-over, including installation of a new scaler, timer, ratemeter, and detector high voltage power supply, (all Hamner Electronics, of AEC-NIM compatible type), was completed one year ago [3, p.46]. During the past year the scintillation detector and preamplifier, flow detector preamplifier, linear amplifier, and pulse height analyzer were replaced. See Figure 17. The purpose of this replacement, using solid-state signal processing electronics, was to

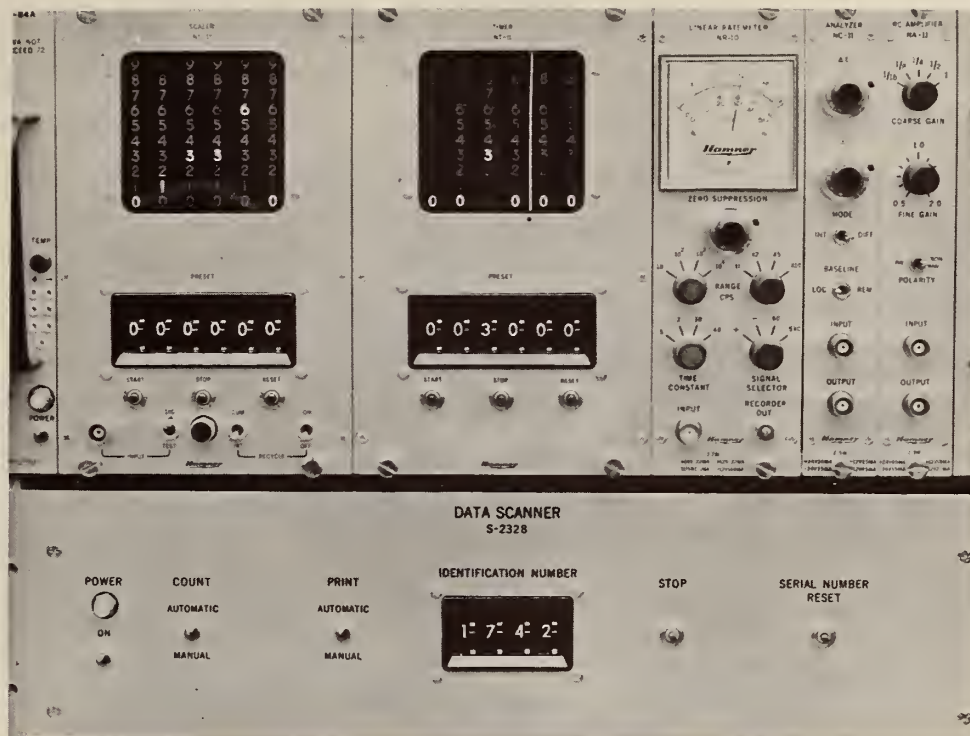


Figure 17. X-ray fluorescence analog and digital signal processing electronics. (The lower panel interfaces the digital electronics to a teletypewriter and paper tape perforator.)

eliminate difficulties with noise and excessive dead-time at the preamplifiers and to eliminate problems of noise and drift at the linear amplifier and pulse height analyzer. The performance of the new equipment has been very satisfactory and no malfunction has occurred since installation. During more than 80% of the past year the single-channel spectrometer has been operated on a 40 hours per week basis.

An interface unit (the Hamner Data Scanner) was added last July to link the scaler and timer of the single-channel spectrometer to a teletype printer and tape punch. This system permits automatic data logging in a form (paper tape) which is computer-compatible. Figure 18 illustrates the

format of output of this device; data tapes such as this one have been processed both on the GE-265 time-sharing computer and on the UNIVAC 1108 computer.

**2-16-68 DET OF MN KA IN CAST STEEL
AND DUCTILE IRON.**

0001	1178	301990	010000
0002	1174	075850	010000
0003	1176	226139	010000
0004	1177	146695	010000
0005	1178	299408	010000
0006	1179	234217	010000
0007	1180	386691	010000

Figure 18. Teletypewriter print-out produced by digital interface. (The columns, from left to right, are: serial number, specimen number, number of counts, and time in hundredths of a second.)

Plans for future changes in the single-channel spectrometer include a light element conversion for the flow proportional detector. This conversion will consist of installation of a deburred collimator and polypropylene window in order to improve our capability for determining sodium, magnesium, aluminum, and silicon.

The valuable assistance of Mr. A. M. McDermott of the NBS Electronic Instrumentation Section in the installation of new electronics is gratefully acknowledged.

B. Research Activities

The manuscript "X-Ray Fluorescence Analysis of Silver Dental Alloys with Correction for a Line Interference" was published [14].

A brief description of our research into the interelement interference problems in x-ray fluorescence analysis was given earlier [3, pp 45, 48]. This work is continuing and will be applied to the analysis of five projected high-

temperature alloy and nickel-base electronic alloy SRM's. As a part of this study the computing portion of a rather flexible computing program, IEMAT, has been completed and is now ready for testing. This program will allow comparison of the Lucas-Tooth technique with other similar empirical correction techniques by application to common sets of data. Input-output sections and documentation for IEMAT are yet to be developed.

Several programs used in x-ray fluorescence analysis are listed in Table 2 according to the function of the program. The programs which are written in the BASIC language for the GE-265 computer have been documented and were recently issued in a Technical Note [4].

Table 2. Programs used in x-ray fluorescence analysis.

<u>Function of program</u>	<u>Program name</u>	
	<u>GE-265</u> <u>(BASIC)</u>	<u>UNIVAC 1108</u> <u>(FORTRAN V)</u>
Homogeneity testing including analysis of variance	XRAY1	CODEAV (Modified for paper tape data entry)
Analytical calibration (No interelement effects accounted for)	CFIT2	ORTHO (Called through OMNITAB)
Analytical calibration (Interelement effects accounted for)	--	IEMAT ^a
Frequency distribution and time-trend analysis	--	FREDIS
Plating thickness calibration, analysis and report generation	PLATE1 PLATE2	--
Generally applicable data loading, sorting, writing and statistical programs	STAT SORT COLS8 WRITE	PTLOAD CPUNCH MTPRNT GRAFIC PLOT

^aStill under development and testing.

C. Examples of Applications

X-ray fluorescence spectrometry has been applied to the analysis of a wide variety of materials this year. The range of materials is illustrated by considering the types characterized for the SRM program; these have included white cast iron, glass, transformer steel, ferrosilicon powder, cast steel, ductile iron, high temperature alloys, and electronic and magnetic alloys.

An example of effective analytical support to the production of an SRM is given by the data in Table 3. In this example inhomogeneity was observed for Mn in a batch of ferrosilicon powder received at NBS and intended to be SRM 59a.

Table 3. X-ray fluorescence determinations of manganese in ferrosilicon powder.
(Mn, in percent)

	<u>Date and treatment</u>			
	9/1/67	2/7/68 ^a	3/15/68 ^a	3/22/68
<u>Position</u>	<u>As received.</u>	<u>Can shaken for 8 hrs.</u>	<u>Sieved at 100 mesh and twice mixed in a motorized mixer for 1/2 hr.</u>	<u>No further treatment. Final homo- geneity study.</u>
Top	0.62	0.6	0.79	0.79 ₅
Middle	0.73	0.8	0.80	0.79 ₅
Bottom	1.12	1.1	0.81	0.80 ₅
Error	0.01 ^b	--	--	0.005 ^c

^aThese intermediate tests were made only to determine if a full test of homogeneity was warranted as a result of the treatment; because of the limited nature of the data, no error analysis was made.

^bTwo times the standard deviation of the mean of four determinations.

^cTwo times the standard deviation of the mean of five determinations.

A series of treatments was set up by the SRM office to improve the homogeneity. Redetermination of homogeneity immediately following each treatment, provided systematic reports on the status of the material and indicated a point for termination of the treatments.

An interesting observation concerning specimen surface preparation arose in the analysis of cast steel SRM 1138, 1138a, 1139, and 1139a and ductile iron SRM 1140, 1140a, 1141, 1141a, 1142, 1142a. In these specimens manganese, silicon, copper, nickel, chromium, vanadium, molybdenum, titanium, and arsenic were determined relative to previously certified SRM's of similar type. The surfaces of the specimens and standards were prepared by polishing on successively finer silicon carbide paper, through 600-mesh grit. Polishing was completed with a 6- μ m diamond finish. Our initial assumption was that the material was hard enough so that grinding with silicon carbide would not affect the determination of silicon because of imbedding. Data from independent analyses have supported this assumption in the case of the ductile iron specimens; however, for the cast steel specimens, x-ray fluorescence consistently yielded a higher value than other methods (approximately 15% higher in the case of 1138 and 1138a). The specimens and standards were repolished with aluminum oxide papers and aluminum oxide slurry for finishing. Results for analyses following the two preparation methods are given in Table 4. The values obtained with the aluminum oxide method are in close agreement with independent determinations, lending support to the conclusion that this method is more accurate. Reexamination of the physical properties of these materials confirms that 1138 and 1138a is unusually soft (untypical of normal cast steel hardness) and this may be the cause of the silicon contamination.

Table 4. X-ray fluorescence determinations of
silicon in cast steel.
(Si, in percent)

<u>Specimen</u>	<u>Preparation method</u>	
	<u>Silicon carbide A^a</u>	<u>Aluminum oxide B^b</u>
1138	0.42	0.36
1138a	0.30	0.25
2x(Std. Dev.)	0.014	0.014
1139	0.88	0.84
1139a	0.82	0.80
2x(Std. Dev.)	0.026	0.026

^aMethod A, polishing with 600-mesh silicon carbide paper followed by a 6- μ m diamond finish.

^bMethod B, repolishing with aluminum oxide papers followed by aluminum oxide slurry.

Valuable contributions to the analyses mentioned in this section have been made by the following personnel: Martha M. Darr assisted in the analyses of cast steel and ductile iron SRM's, Doward M. Bouchette has performed quantitative analyses and tests of homogeneity, Chong K. Kim performed the initial tests of glass homogeneity, Clarence W. Gifford assisted in the homogeneity testing of ferrosilicon powder, and James L. Izlar assisted in specimen identification and label checking by x-ray methods.

Fielding Ogburn, Jacob Smit, and Virginia Pennington (from the Metallurgy Division) have been part-time guest workers carrying out a project of thickness measurements on electroplated metal coatings as discussed in an earlier report [3].

S. D. Raspberry

5. SPARK SOURCE MASS SPECTROMETRY

Efforts during the past year with the spark source mass spectrometer have contributed to better understanding of the factors affecting accuracy of analysis and means of improving analytical techniques. Studies of the uniformity of sensitivity of the photographic plate, used as detector, have indicated that this is an area that can have significant effect on the accuracy of analysis. In methods development, stable isotopic dilution analysis has been extended to the determination of elements at very low concentrations, for example, tin at 20 ppb* in zinc. This sensitive technique has been applied to the certification of impurities in two zinc standards (SRM 728, 683) and a platinum standard (SRM 681), all three of which contain levels of impurities that would make them useful standards for spark source work. Several computer programs have been written to improve the speed and accuracy of analysis and to compare the usefulness of several different plate calibration functions and modifications thereof. Emphasis has been placed on working with materials that can serve as standards for the spark source mass spectrometer.

A. Instrument Improvements

Magnetic shim stocks 0.003 in. thick inserted behind the ion sensitive plates have been used in the plate holders in order to decrease certain types of plate background. This shim has been quite effective in lowering background; however, the attraction of the magnetic material to the pole faces of the magnet results in a force that bows the plate toward the magnet. This displacement, which occurs on the two ends of the plate and in the center between the two hold down tabs, apparently varies as the plate is racked

* In this report ppb indicates parts per billion by weight (ng/g) and ppm indicates parts per million by weight (µg/g).

from exposure to exposure. This change in displacement results in variation of position of the plate with respect to the magnet face. Line position and focus are dependent on plate position and the effects are largest at the low mass and smallest at the high mass ends of the plate. The combined effects have been to yield plates having lines at mid-position and low position displaced with exposure position, and with the low mass lines at somewhat less than optimum focus. Modifications were made to the plate holders to overcome these problems. Figure 19 shows at the top the original plate holder design for our instrument (C.E.C. Model 21-110). The bottom plate holder shows the extra pair of tabs

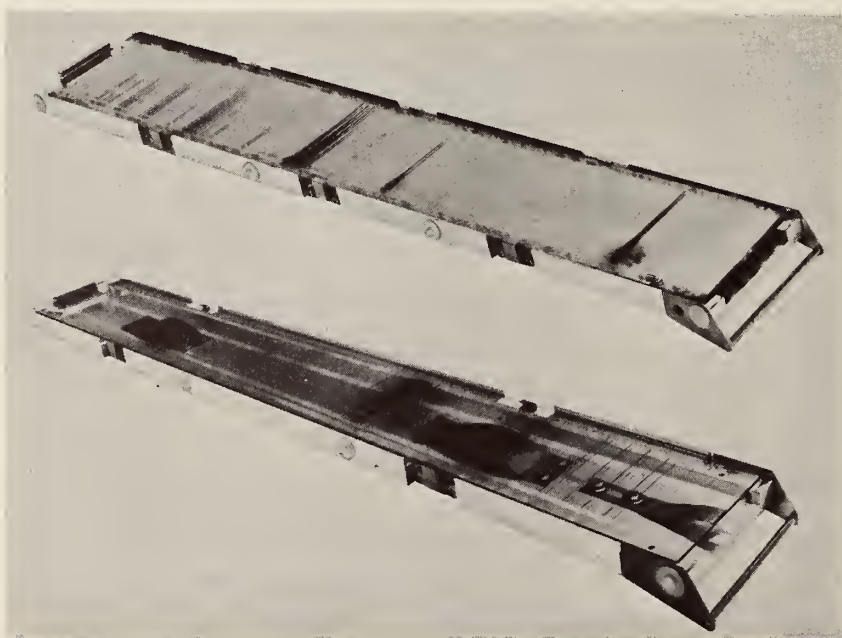


Figure 19. Plate holders for mass spectrograph. (Top, original plate holder; bottom, plate holder with magnetic shim and tabs.)

added to the center of the plate holder and the tab added to the low mass end of the holder. These tabs prevent the plate from uncontrolled bowing and with these modifications the

previously mentioned symptoms have disappeared. With four hold-down tabs instead of the previous two we can now have a controlled bend in the plates to obtain better focus. Previous focusing experiments have indicated that a bend in the plate would be required to obtain optimum focus at the low mass end of the plate.

P. J. Paulsen, D. E. Kelleher

B. Homogeneity of Ion Sensitive Emulsions and Precision of Ion Beam Measurements

1. Introduction

The precision and accuracy with which the chemical analysis of materials can be made by mass spectrometry is determined by (1) the precision with which mass analyzed ion beams can be measured, (2) the accuracy with which ion beam ratios can be measured, and (3) the precision and accuracy of the numerical information on the degree by which the ion sample, presented to the mass spectrometer detector, represents the composition of the solid sample.

In spark source mass spectrometric analysis of solids, particularly for trace quantities, these precision and accuracy problems take the following form. In the ion beam measurement, it is the precision with which this can be done photographically. The ion beam ratio measurement is a combination electrical and photographic problem. The degree of representation is determined by measurements with standard samples.

2. Method

To determine the precision achievable in the photographic measure of an ion beam, a series of replicate exposures was made in which the successive mass spectra covered nearly the full 5-cm width and extended over a 15-cm length of the Q-2 emulsion.

The major component rather than a minor component of a solid sample should be recorded in the replicate exposures. This circumvents fluctuations that might be caused by sample inhomogeneities and/or variations in degree of representation of the specimen composition by the ion sample.

Platinum is a very suitable material for these replicate tests. By utilizing the low abundance isotopes of mass 190 and 192, the exposure -- an electrical measurement of charge at the monitor electrode -- can be replicated with greater precision than with an element that had no low abundance isotopes. Other desirable properties of platinum will be indicated in the section on results.

The Q-2 emulsion measure of the platinum ions is made by integrating [2, p. 62] the ion intensity profile of the mass line in question.

3. Results

Table 5 presents representative data from 21 replicate exposures made at a given value of the magnetic field, by racking the plate holder in the usual way. N^{+1} derived from the above integration represents the number of singly charged ions of the platinum isotope of mass 190. N^{+2} represents the number of doubly charged ions of the same platinum isotope. $N^{+1} + N^{+2}$ is a good approximation of the total number of platinum ions to the Q-2 detector since the ions of charge greater than +2 are negligible. $N^{+1}/(N^{+1}+N^{+2})$ gives the fraction of the total represented by N^{+1} . The average value for N^{+1} has a relative standard deviation of 4.3% and that for $N^{+1}+N^{+2}$ is 4.6%. This indicates that the fluctuations in N^{+2} do not compensate those in N^{+1} . Moreover, the fraction of the total represented by N^{+1} is a nearly constant one -- 0.90 with 1.3% relative standard deviation. Consequently, $N^{+1}/0.90$ is an adequate measure of the total ionization and the precision in the N^{+1} average is an adequate measure of the precision with which the total ionization is known.

Table 5. Ion beam measurements on 21 replicate mass spectra of platinum. (N^{+1} and N^{+2} represent the singly and doubly charged ions)

<u>Exposure No.</u>	<u>N^{+1}</u>	<u>N^{+2}</u>	<u>$N^{+1}+N^{+2}$</u>	<u>$N^{+1}/(N^{+1}+N^{+2})$</u>
1	1590	205	1795	0.886
2	1482	198	1680	.882
3	1490	187	1677	.889
4	1515	171	1686	.898
5	1525	236	1761	.865
6	1460	171	1631	.894
7	1485	185	1670	.889
8	1425	163	1588	.897
9	1483	163	1646	.902
10	1409	155	1564	.900
11	1444	156	1600	.902
12	1442	154	1596	.904
13	1486	145	1631	.910
14	1375	151	1526	.900
15	1435	153	1588	.904
16	1366	164	1530	.892
17	1348	166	1514	.890
18	1417	160	1577	.897
19	1475	165	1640	.899
20	1490	146	1636	.911
21	1585	142	1727	.918
Average	1464	168	1632	.896
Std. Dev.	4.3%	13.6%	4.6%	1.3%

Data like that of Table 5 reveal the widthwise homogeneity of the Q-2 emulsion but tell nothing about how the emulsion sensitivity may vary lengthwise on the plate. This was investigated with replicate exposures made at different values of the magnetic field. Three typical plates are represented in the three-dimensional drawing of Figure 20 in which a 5- by 16-cm emulsion is portrayed. At each of the 12 magnetic field settings, 12 replicate spectra were recorded widthwise by racking the plate in the usual manner. Each of these spectra is suggested by a single short line on the emulsion in the XZ plane.

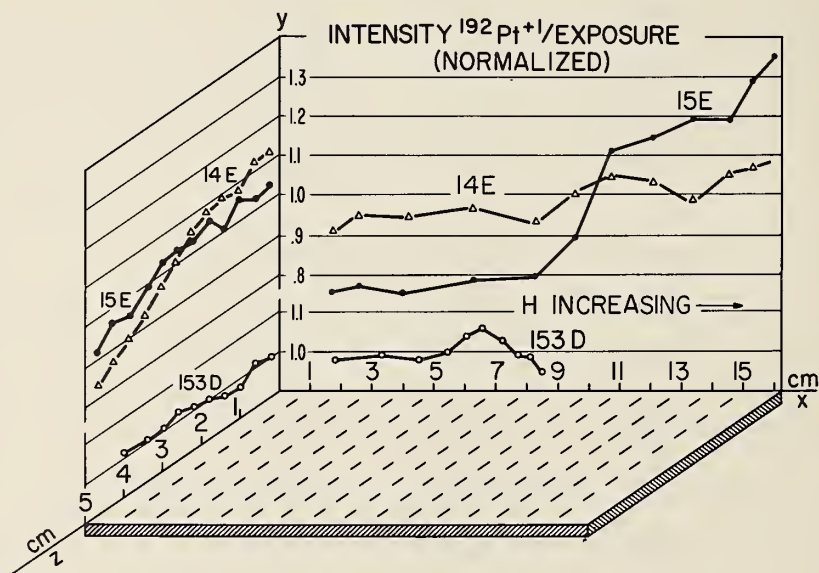


Figure 20. Ion beam measurements on platinum mass lines. (Replicate spectra extending widthwise and lengthwise on Q-2 ion sensitive emulsions.)

These curves delineate averages made as follows. In the lengthwise ones all the data at each racking position were averaged. In the widthwise curves, all the data at each magnetic field were averaged. The individual curves

do not seriously disagree with the average curves for a particular plate.

For plate 153D, the emulsion measure of the ion beam is quite constant both lengthwise and widthwise. Plate 14E shows a 20% trend lengthwise and a 30% trend widthwise. Plate 15E shows a trend of about 10% widthwise but a large overall change of 60% lengthwise.

The ZY curves clearly show the widthwise variation in the emulsion sensitivity. The XY curves are not so easily interpreted. When the magnetic field is increased, the length of the trajectory of the platinum (+1) ions is decreased. Consequently, the Z axis spread -- the ion spreading by radial projection in the unfocused direction -- decreases, and the number of ions/cm² producing the mass line increases. Thus, the emulsion measure of the ion beam is determined by two factors, the Z axis spread factor which increases with magnetic field, and the emulsion sensitivity factor, for which the lengthwise variation is not predictable.

The Z axis spread factor F can be experimentally measured by recording replicate spectra at several values of magnetic field, and then, after reversing the Q-2 plate in its holder, recording a second set of replicates. Thus, in one set of replicates, the factor F increases to the right of the reference end of the plate whereas in the other set, F decreases.

Tests of this sort indicate that, for the spark source mass spectrograph being used (21-110), this Z axis spread factor F amounts to about 20% over a 20-cm length of ion sensitive plate, the standard plate being 38 cm long in this instrument.

4. Circumvention of Inhomogeneities in Ion Sensitive Emulsions

When samples are being compared, their spectra can be interspersed to neutralize widthwise variations in emulsion

sensitivity. When a conventional graded series of exposures is being made, the exposures can be interspersed with replicate spectra of platinum to determine the magnitude of the correction factor introduced by a widthwise inhomogeneity.

Lengthwise inhomogeneities can be offset by measuring the Z axis spread factor for the spark source mass spectrometer being used, and then recording appropriate replicate spectra on the plate containing the spectra of the sample under analysis.

5. Summary and Interpretation of Results

a. The total number of platinum ions to the plate and the precision of this quantity can be derived from measurements on the isotopic mass line of the singly charged ion of mass 190.

b. Tests with Q-2 plates from different lots indicate that the sensitivity fluctuations about an average may be $\leq 5\%$ standard deviation in a 5-cm length, or there may be as much as a 30% change in sensitivity over this distance.

c. Techniques for circumventing emulsion inhomogeneities may be effective.

A. J. Ahearn

C. Stable Isotopic Dilution Analysis of Pure Materials Using Preconcentration Techniques

1. Zinc

The stable isotopic dilution analysis of NBS zinc composition standards SRM 683 and SRM 728 for Pb, Tl, and Cd reported previously [3] has been extended to the determination of Sn, Ag, and Cu in the same material. The combined use of preconcentration techniques and measurement of isotopic ratios by a spark source mass spectrograph has enabled us to determine 20 ppb of tin in these samples. The relatively constant detection sensitivity of all elements by spark

sources would predict a similar low detection level to any element amenable to analysis by stable isotopic dilution. The other elements determined in these zinc samples in fact gave signal intensities that indicated that they too could have been determined as low as 20 ppb. Table 6 gives the results of analysis of the zinc bar for silver and tin. The two sets of values listed come from completely independent runs starting with new spiking solutions.

Table 6. Isotopic dilution determinations of silver and tin in four samples of zinc SRM 683

ppm by weight				
<u>Elements and run</u>	<u>Samples</u>			
	<u>1 A</u>	<u>1 B</u>	<u>2 A</u>	<u>2 B</u>
Silver 1	1.18	1.06	1.13	1.02
2	<u>1.14</u>	<u>1.18</u>	<u>1.33</u>	<u>1.25</u>
Av.	1.16	1.12	1.23	1.14
Tin 1	0.019	0.018	0.013	0.016
2	<u>.023</u>	<u>.019</u>	<u>.014</u>	<u>.016</u>
Av.	0.021	0.019	0.014	0.016

Three lots of zinc shot SRM 728 and both ends of two bars of zinc SRM 683 were run. The results are given in Table 7. The close agreement between the two samples for all the elements arises from the fact that both samples were produced from a common batch of zinc.

2. Platinum

Spark source stable isotopic dilution analysis has also been applied to the determination of elements in a doped platinum sample SRM 681. The impurities were concentrated

Table 7. Average copper, silver, and tin concentrations in shot and bar samples of zinc.

ppm by weight

<u>Samples</u>	<u>Elements</u>		
	<u>Copper</u>	<u>Silver</u>	<u>Tin</u>
SRM 728 (Shot)	5.54	1.16	0.021
Precision ^a	<u>±.49</u>	<u>±.05</u>	<u>±.009</u>
SRM 683 (Bar)	5.59	1.16	0.017
Precision	<u>±.26</u>	<u>±.12</u>	<u>±.001</u>

^aPrecision values are 95% confidence interval for the mean, $(t_{.95} S)/\sqrt{n}$. For SRM 728, n is 6; for SRM 683, n is 8.

by use of cation exchange columns. The actual preconcentration and spiking procedures used on the platinum and zinc samples are described by R. Alvarez in Section 6 of this report. Table 8 lists the values found by isotopic dilution along with the final certified values and spark source values calculated by other means in order to contrast the capabilities of these techniques. In the second column are listed the impurity concentrations computed without the benefit of a standard. In this case the elements were all assumed to have the same atomic sensitivity as platinum when determined by measurement of the Pt 190 isotope. Corrections were made for line width variation, isotopic abundances, and the variation of plate sensitivity with mass. The third column lists values determined by comparison to a platinum sample of known composition. The impurity levels in this "comparison standard" ranged from 0.06% Cu (600 ppm) to 0.194% Ir (1940 ppm). Thus the standard sample contains roughly 100 times the impurity concentration as the "unknown" Pt 681. The next column gives the spark source isotopic dilution results and

the last column the final certified values. The certified values represent results from a number of methods; however, the only values from the spark source entering into the certified values are those from the isotope dilution determinations.

Table 8. Comparison of results of three types of mass spectrographic analyses to certified values for Pt 681

ppm by weight

<u>Element</u>	<u>No standard</u>	<u>1000 ppm standard</u>	<u>Isotope dilution SSMS</u>	<u>Certified by NBS</u>
Mg	48	8.6	--	12
Ca	27	11	--	--
Fe	9.7	--	--	5
Ni	--	--	.46	.5
Cu	20	3.0	5.04	5.1
Zr	12	--	--	11
Rh	18	8.4	--	9
Pd	17	8.8	5.92	6
Ag	15	2.5	2.09	2.0
Ir	--	12	--	11
Au	--	20	--	9
Pb	94	14	13.6	12

A comparison of results indicates the isotope dilution values are in good agreement with the certificate value and therefore with the other techniques. The comparison to the "standard" sample does quite well considering that the standard used contained 100 times the impurity level; gold is the only element that can be considered to be in significant error. Without the comparison standard however, positive errors as

high as a factor of 8 (for lead) were obtained using the matrix sensitivity factor as is shown in column two.

D. Plate Calibration Functions

Two computer programs have been written to calculate calibration curves from data with background readings via iterative computation. Both use the method of least squares and are designed to use known isotope ratios of elements to calculate plate response. The first program uses a fourth power polynomial to fit the plate calibration curve "shape". The second assumes a probability function response and two modifications thereof. These are, where b and c are the modifications:

- (a) $\log \text{ intensity} = K_1\chi + C$
- (b) $\log \text{ intensity} = K_1\chi + K_2\chi^2 + C$
- (c) $\log \text{ intensity} = K_1\chi + K_3\chi^3 + C$

where χ is the probability value of the percent absorption and K_1 , K_2 , and K_3 are plate constants to be determined.

The polynomial equation and the addition of $K_2\chi^2$ and $K_3\chi^3$ terms to our normal plate function of $K_1\chi + C$ are attempts to allow more leeway in the "shape" of the function used to fit the calibration data. Although the four-term polynomial can fit the calibration data as well as or better than the probability function, it will fit the plate response only over the range covered by the calibration data. It cannot predict plate response outside of this tested range. The probability function, Seidel equation, and the Hull equation on the other hand predict reasonable response outside of their tested range since in each case their "shape" is fixed. For this reason polynomials have not been adopted to represent plate response curves. Use of $K_2\chi^2$ or $K_3\chi^3$ terms must result in a closer fit to the true calibration curve. However, a limited testing of the three versions of the probability equations has shown only a small improvement with the additional terms. Indications are that the equation

$[\log(\text{intensity}) = K_1 \chi + C]$ fits the plate response well enough so that any discrepancies in fit are obscured by variations in plate uniformity.

The effects on the calibration curves of setting the microphotometer zero per cent absorption at plate background or at a portion of the plate cleared by fixing before development were studied. For the polynomial these two cases are mathematically identical. The three forms of the probability equation showed changes in K values with this shift in zero; however, there was no significant difference in the precision of fit to the calibration data with the zero shift. Since adjustment of zero to the background level is so difficult to duplicate on the same plate at two different times, the use of the cleared plate zero has been adopted.

E. New Computer Programs

New programs have been written for the time-shared computer for use with the spark source. An outline of some of the most frequently used programs is given here.

1. Program PPMCAL

Purpose - To calculate impurity concentration from data obtained from a plate, based either on information from a standard sample or on the plate sensitivity to the matrix element.

Input data - Unit mass of isotope used, abundance of isotope, exposure levels used and line areas measured for the "standard", "unknown", and matrix plus concentration of standard if available.

Output data - Concentration of unknown in ppm by weight and atomic, and \pm the 95% confidence interval on the limiting mean.

The results are based on the geometric mean, with the confidence interval calculated from the variation in the unknown and the standard (or the matrix) data. If a standard is not available the results are calculated from sensitivity

factors based on matrix sensitivity corrected for isotopic abundances and variation in plate sensitivity with mass.

2. Program PAIRS

Purpose - To test for homogeneity among n sets of duplicate samples; to compute statistics on isotope dilution analysis.

Input - Computed concentrations on independently analyzed duplicates of several samples.

Output - Statistics to indicate:

- a. overall precision of analysis, and
- b. if the differences among samples indicate inhomogeneities.

3. Program SENSAT

Related to PPMCAL in form and input data. Uses sensitivity data from several elements in a standard sample to calculate an average plate sensitivity factor to be used for elements without a standard. This value is then fed into PPMCAL to replace the matrix sensitivity value.

P. J. Paulsen, D. E. Kelleher

6. ANALYSIS OF HIGH PURITY MATERIALS

Our initial experimentation in applying isotope dilution-preconcentration techniques to the spark source mass spectrometric determination of trace elements was outlined in last year's annual report [3]. This project is conducted as a joint investigation with P. J. Paulsen who describes the spark source mass spectrometer activity in Section 5 of this report.

The principal features of these isotope dilution-preconcentration methods are:

1. The results are unaffected by "sorption" and mechanical losses once the isotopic additions ("spikes") have been made and equilibrium established.
2. A determination of the recovery or yield of the trace elements is unnecessary.
3. Since the high voltage spark source ionizes all elements, multi-element trace determinations can be made simultaneously.
4. The preconcentration features of these methods provide higher intensities for the isotopic mass lines.

Since contamination from reagents, vessels, chemical operations, and environment constitutes the principal limitation of the method, our efforts are directed toward developing techniques which minimize this contamination. Our objectives are to make reliable trace determinations particularly at concentrations of less than one ppm with the main area of applications being the analysis of materials designed to serve as NBS Standard Reference Materials for trace analysis. Examples of these methods are discussed below:

A. Zinc

The method developed for the determination of Pb, Cd,

and Tl in zinc [3] was extended to the determination of Ag, Cu, and Sn in the same matrix. These six elements, determined simultaneously, in Zinc NBS Standard Reference Materials 683 and 728, ranged from 11 ppm for Pb to 20 ppb for Sn. The isotopically enriched trace elements were electrodeposited from a solution of the zinc onto high-purity gold wires using the cell shown in Figure 21. The cell body, made of polytetrafluoroethylene polymer, had been used previously [16] to electrodeposit Ag onto the surface of a spectroscopic graphite electrode from a zinc solution. This technique had been proposed as a preconcentration method for

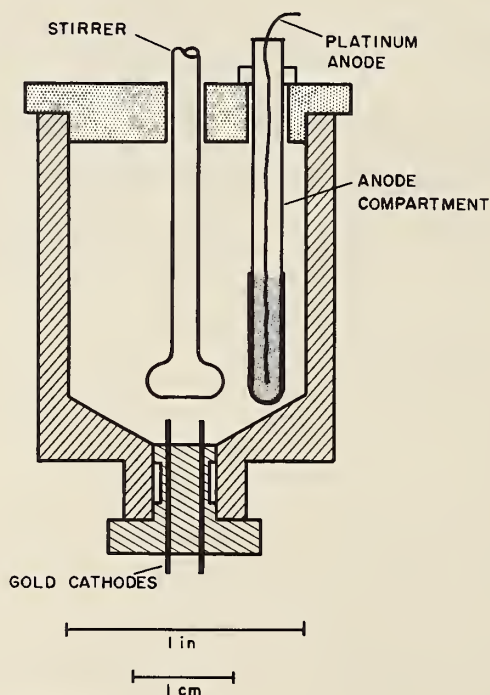


Figure 21. Electrodeposition cell.

optical emission spectroscopy. For the isotope dilution work, the graphite electrode was replaced with a Teflon plug of the same diameter through which two gold wires had been inserted to serve as the cathode. The Pt-Ru tubing was

replaced with a separate anode compartment to avoid generating Cl_2 from the HCl electrolyte.

During a series of experiments, it was observed that the first sample of zinc gave a higher result for Sn than succeeding samples from the same source. An aliquot of this first sample run twelve days later gave a result that was in agreement with the other samples. The ^{117}Sn , added as the "spike", had been obtained from the Oak Ridge National Laboratory as SnO_2 , dissolved in HCl , and diluted with 6M HCl to a concentration of $0.04\mu\text{g/ml}$. The possibility that, for the first sample, equilibrium had not been attained between the Sn from the sample and the ^{117}Sn spike was indicated. Consequently, the procedure was modified to add the isotope solutions at the early stages of sample dissolution rather than at the end of this step. Moreover, since the ^{117}Sn solution was so dilute, i.e. $0.04\mu\text{g/ml}$, there was concern that "sorption" losses could have reduced the actual amount of "spike" added. Therefore, for a second set of samples which were run, 1 part of ^{117}Sn spike was added to 100 parts of high purity zinc to increase the total ion concentration. At this ratio, the impurities in the zinc were too low to interfere with the elements being analyzed. In addition, the tin spike was added from a solution of $0.4\mu\text{g/ml}$, a ten-fold increase in concentration, and the volume added was reduced proportionately. Good agreement was obtained between the two sets of results. The $0.4\mu\text{g/ml}$ ^{117}Sn solution was assayed by spiking with a known amount of normal tin and found to be 93% of its original concentration eleven days after it had been used to spike the samples.

B. Platinum

A method was developed to determine Ag, Cu, Pb, Pd, and Ni simultaneously in an NBS Standard Reference Material of Platinum, No. 681. Since a manuscript detailing the method has been prepared for publication, only an outline

is presented here. A weighed sample is dissolved in aqua regia and solutions of stable isotopes are added. The solution is then evaporated to dryness, the salts dissolved in water and the solution passed through a cation exchange column. The isotopically enriched trace elements are retained on the column and the platinum passes into the effluent as chloroplatinate anion. After washing the column, the trace elements are eluted with 3M HCl into an electrolysis cell and NH_3 added to neutralize the acid. The trace elements are then electrodeposited onto gold wires. This procedure has several advantages: (1) an adherent sample form particularly suited to spark source mass spectrometry is provided; (2) the sample form is attained with a minimum of handling and possible contamination; and (3) the trace elements in elemental form provide a simpler spectrum thus reducing the possibility of interferences. The gold wires are then sparked in the mass spectrometer and the mass spectrum recorded photographically. The results are calculated from the isotope ratio measurements, the sample weight, the weight of the separated isotopes ("spikes") added, the isotope abundances of the separated isotopes and the natural abundances (except for lead). For lead, the abundance varies in nature and must be measured for each material.

The results, shown in Table 9, were in good agreement with other analytical methods as indicated by the "estimated accuracy" of the certificate values. For Ni, an "estimated accuracy" of the results was not made since the determination had not been made by another method with sufficient precision. Other elements listed on the certificate are not shown.

C. Gold

Work is in progress to determine Fe, Ag, Cu, and possibly In simultaneously in samples of high purity gold. Although employing essentially the techniques developed for the analysis of platinum, the concentration levels of these

Table 9. Concentrations determined by
isotope dilution in Platinum SRM 681

ppm by weight

<u>Element</u>	<u>Isotope dilution</u>	<u>Certificate value^a</u>	<u>Estimated accuracy of certificate value^a</u>
Ag	2.09	2.0	Within 0.5 ppm of actual value
Cu	5.04	5.1	" 0.5 " " " "
Pd	5.92	6	" 1 " " " "
Pb	13.6	12	" 2 " " " "
Ni	0.46	0.5	

^aSee copy of certificate reproduced in the Appendix to this report.

elements (Fe 0.2 ppm, Ag 0.1 ppm, Cu 0.1 ppm and In <0.1 ppm) has made their precise determination difficult because of contamination problems. The blanks are evaluated by spiking reagents with the stable isotope solutions and going through all of the steps of the procedure.

R. Alvarez

7. PERSONNEL AND ACTIVITIES

A. Personnel Listing

Spectrochemical Analysis Section

Bourdon F. Scribner, Section Chief
Arthur J. Ahearn, Research Physicist
Karen L. Loraski, Section Secretary

Group I. Optical Spectrometry

Marvin Margoshes, Chemist
Claude Veillon, Post Doctoral Research Chemist
(Terminated)
Joseph L. Weber, Physicist
Martha M. Darr, Chemist
Virginia C. Stewart, Chemist
Doward M. Bouchette, Physical Science Technician

Group II. X-Ray Spectrometry and Electron Probe Microanalysis

Kurt F. J. Heinrich, Chemist
Ping-Kay Hon, Chemist
Donald L. Vieth, Physical Metallurgist (On extended
leave)
Stanley D. Rasberry, Physicist
Mary Ann Giles, Chemist (Terminated)
Chong K. Kim, Chemist (Summer 1967)
Charles E. Fiori, Electronic Technician

Part Time Guest Workers:

Harvey Yakowitz, NBS Metallurgy Division
David Carpenter, National Institutes of Health
Fielding Ogburn, NBS Metallurgy Division
Jacob Smit, NBS Metallurgy Division
Virginia H. Pennington, NBS Metallurgy Division
Michael Duke, Geological Survey

Group III. Spark Source Mass Spectrometry

Paul J. Paulsen, Chemist
Daniel E. Kelleher, Chemist

Part Time Guest Worker

Clemente Noutary, Atomic Energy Commission
Argentina

Group IV. Enrichment Techniques

Robert Alvarez, Chemist

B. Publications

1. Ahearn, A. J.
Spark Source Mass Spectrometer Measurements of Dopants of Known Concentrations in Gallium Phosphide, Anal. Chem. 39, No. 3, 350-352, (1967).
2. Ahearn, A. J.
Spark Source Mass Spectrometric Analysis of Solids, in "Trace Characterization, Chemical and Physical", National Bureau of Standards, Monograph 100, April 1967, p. 347.
3. Heinrich, K. F. J., and Giles, M. A. M.
X-Ray Wavelength Conversion Tables and Graphs for Qualitative Electron Probe Microanalysis, NBS Technical Note 406, Sept. 25, 1967.
4. Eick, J. D., Caul, H. J., Smith, D. L., and Rasberry, S. D.
Analysis of Gold and Platinum Group Alloys by X-Ray Emission with Corrections for Interelement Effects, Appl. Spectry. 21, No. 5, 324-328 (1967).
5. Margoshes, M.
Selection of Wavelengths for Atomic Absorption Spectrometry, Anal. Chem. 39, No. 10, 1093-1096 (1967).
6. Heinrich, K. F. J.
Electron Probe Microanalysis by Specimen Current Measurement. X-Ray Optics and Microanalysis, Hermann Eds., Paris, 1966, p. 159 (Appeared in fall of 1967).
7. Scribner, B. F. (Editor)
Activities of the NBS Spectrochemical Analysis Section, July 1966 through June 1967, NBS Tech. Note 422, Jan. 1968.
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Solid-state Energy-dispersion Spectrometer for Electron Microprobe X-ray Analysis, Science 159 528-529 (1968).
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The Impact of Computer Techniques on Atomic Spectroscopy (A summary), XIII Colloquium Spectroscopicum Internationale, Ottawa June 1967, (Published Jan. 1968) p. 97.

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Properties of the Laser Probe with Rotating Prism
and Liquid Q-Switches (A summary), Ibid p. 156.
11. Veillon C., and Margoshes, M.
Atomic Absorption and Atomic Fluorescence Spec-
trometry with a Plasma Torch (A summary), Ibid p. 281.
12. Heinrich, K. F. J.
Inhomogeneity Studies of Alloys with the Electron
Microprobe (A summary), Ibid p. 421.
13. Alvarez, R.
The Spectrochemical Determination of Ultra-Trace
Elements in High-Purity Metals by Preconcentration
Using Matrix Volatilization (A summary), Ibid p. 454.
14. Rasberry, S. D., Margoshes, M., and Scribner, B. F.
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trochemistry Laboratory; Optical Emission and X-ray
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Quantitative Electron Probe Microanalysis: Absorp-
tion Correction Uncertainty, Microchim. Acta 1968,
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16. Rasberry, S. D., Caul, H. J., and Yezer, A.
X-Ray Fluorescence Analysis of Silver Dental Alloys
with Correction for a Line Interference, Spectro-
chimica Acta 23B, No. 5, March, 345-351 (1968).
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Scanning Electron Probe Microanalysis, ASTM Spec.
Tech. Publ. 430 (1968) p. 315.
18. Margoshes, M., and Scribner, B. F.
Emission Spectrometry (A review), Anal. Chem. 40,
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Spec. Publ. 298 (In press).
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Quantitative Electron Probe Microanalysis:
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Common Sources of Error in Electron Probe Microanalysis, Advances in X-ray Analysis, Vol. 11, Plenum Press, N. Y. (In press).
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A Pneumatic Solution Nebulization System Producing Dry Sample Vapor for Atomic Spectroscopy. Spectrochim. Acta, Part B (In press).
23. Veillon, C., and Margoshes, M.
An Evaluation of the Induction-coupled, Radio-frequency Plasma Torch for Atomic Emission and Atomic Absorption Spectrometry, Spectrochim. Acta, Part B (In press).

C. Talks Given

1. Heinrich, K. F. J., "Common Sources of Error in Microprobe Analysis", Proceedings of Annual Conference on Applications of X-ray Analysis, Denver, Colorado, August 10, 1967.
2. Scribner, B. F., "The Role of the Time-Sharing Computer in the Spectrochemical Laboratory", XII International Congress of Pure and Applied Chemistry, Prague, Czechoslovakia, September 5, 1967.
3. Raspberry, S. D., "New Methods of Data Acquisition and Processing in Spectrochemical Analysis", Society for Applied Spectroscopy, Birmingham, Alabama, September 30, 1967.
4. Heinrich, K. F. J., "Electron Probe Microanalysis of Biological Specimens", National Institutes of Health Bethesda, Maryland, October 4, 1967.
5. Margoshes, M., "Spectrochemical Analysis of Small Volumes with the Laser Probe", Eastern Analytical Symposium, New York, New York, November 8, 1967.
6. Scribner, B. F., "Dr. William F. Meggers - A Dedication", Eastern Analytical Symposium, New York, New York, November 10, 1967.
7. Margoshes, M., "Laser Probe Spectrochemical Microanalysis", Society for Applied Spectroscopy, Clarksville, Maryland, February 27, 1968.

8. Scribner, B. F., "Future Standards for Instrumental Analysis", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 6, 1968.
9. Paulsen, P. J., "Spark Source Mass Spectrographic Analysis of High-Purity Zinc by Isotope Dilution and Electrodeposition of Trace Elements", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 7, 1968.
10. Margoshes, M., "An Algorithm for Computer Fitting of Spectrometric Analytical Curves", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 8, 1968.
11. Alvarez, R., "Determination of Trace Elements in High-Purity Platinum by Isotope Dilution, Spark Source Mass Spectrometry", 155th American Chemical Society National Meeting, San Francisco, California, April 1, 1968.
12. Paulsen, P. J., "Spark Source Mass Spectrometry and Its Application to the Analysis of PPM Level Impurities", Mass Spectrometry Discussion Group of Metropolitan Washington, Springfield, Virginia, April 15, 1968.
13. Alvarez, R. "Stable Isotope Dilution and Separation of Trace Elements for Determination by Spark Source Mass Spectrometry", 762nd Meeting of the Chemical Society of Washington, College Park, Maryland, May 3, 1968.
14. Paulsen, P. J., "Standard Reference Materials for Spark Source Mass Spectrometry", 16th Annual Conference on Mass Spectrometry and Allied Topics, Pittsburgh, Penn., May 15, 1968.
15. Ahearn, A. J., "Homogeneity of Ilford Q2 Emulsions and Precision of Ion Beam Measurements in Spark Source Mass Spectrometry", 16th Annual Conference on Mass Spectrometry and Allied Topics, Pittsburgh, Penn., May 16, 1968.
16. Margoshes, M., "Calibration of Photographic Emulsion on a Digital Computer -- A Critical Test of the Method", 7th National Meeting, Society for Applied Spectroscopy, Chicago, Ill., May 16, 1968.
17. Scribner, B. F., "Future Standards for Instrumental Analysis", Seminar: NBS Meets with Pittsburgh Industry, Dept. of Commerce, Pittsburgh, Penn., May 21, 1968.

18. Margoshes, M., "Time-Sharing Computers", 12th Annual May Conference, Cleveland Section of Society for Applied Spectroscopy and American Chemical Society, Cleveland, Ohio, May 22, 1968.
19. Margoshes, M., "Use of Computers in Emission Spectrochemical Analysis", ACS Summer Symposium, Pennsylvania State University, University Park, Pa., June 19, 1968.

D. Committee Activities

B. F. Scribner

Member, ASTM Committee E-2 on Emission Spectroscopy
Member, ASTM Committee E-13 on Absorption Spectroscopy
Member, Program Committee, Eastern Analytical Symposium, 1967
Delegate to Governing Board, EAS, 1968
Titular member, Commission on Spectrochemical and Other Optical Methods of Analysis, International Union of Pure and Applied Chemistry
Member, Advisory Board, Spectrochimica Acta, Atomic Section
Member, International Advisory Board, Colloquium Spectroscopicum Internationale, 1967
Chairman, Nominating Committee, Society for Applied Spectroscopy, 1968
Chairman, Baltimore-Washington Section, SAS, 1967-68
Member, Wavelength Tables Committee, University of Michigan
Member, Analytical Standards Committee, NBS Analytical Chemistry Division
Member, Analytical Services Committee, NBS Analytical Chemistry Division

M. Margoshes

Editor, Spectrochimica Acta, Atomic Section
Member, Publications Committee, Society for Applied Spectroscopy, 1968
Member, Professional Development Committee, Baltimore-Washington Section, SAS, 1967-68
Program Chairman, Baltimore-Washington, Section, SAS, 1967-68

K. F. J. Heinrich

President-Elect, Electron Probe Analysis Society of America, 1968
Assistant Editor, Mikrochimica Acta

A. J. Ahearn

Vice-Chairman, Subcommittee VII, ASTM Committee E-14
on Mass Spectrometry and Allied Subjects
Co-Chairman, Workshop on Spark Source Mass Spectrometry,
NBS, Nov. 1967

P. J. Paulsen

Member, Subcommittee VII, ASTM Committee E-14 on
Mass Spectrometry and Allied Subjects
Co-Chairman, Workshop on Spark Source Mass
Spectrometry, NBS, Nov. 1967

R. Alvarez

Member, ASTM Committee E-2 on Emission Spectroscopy

J. L. Weber

Member, ASTM Committee E-2 on Emission Spectroscopy,
Subcommittees IV, VII, and IX

S. D. Rasberry

Member, Laser Task Group, ASTM Committee E-2

8. ACKNOWLEDGMENTS

We have had the benefit of considerable assistance from persons in other groups and of the supporting services of NBS including library, plant, and shops; these have been invaluable to the operation of a rather complex laboratory. Some individuals who were especially helpful are named below.

Dr. Robert J. Arms of the computer Services Division has provided very useful advice on computer programming problems. Mr. Brian Joiner of the Statistical Engineering Section assisted in problems involving applications of statistics.

Mr. Harvey Yakowitz of the Metallurgy Division has again worked closely with our microprobe group especially on problems of quantitative microprobe analysis.

Mr. John Hettenhouser of the Instrument Shop provided excellent service on careful preparation of samples of standard reference materials for analyses in our Section.

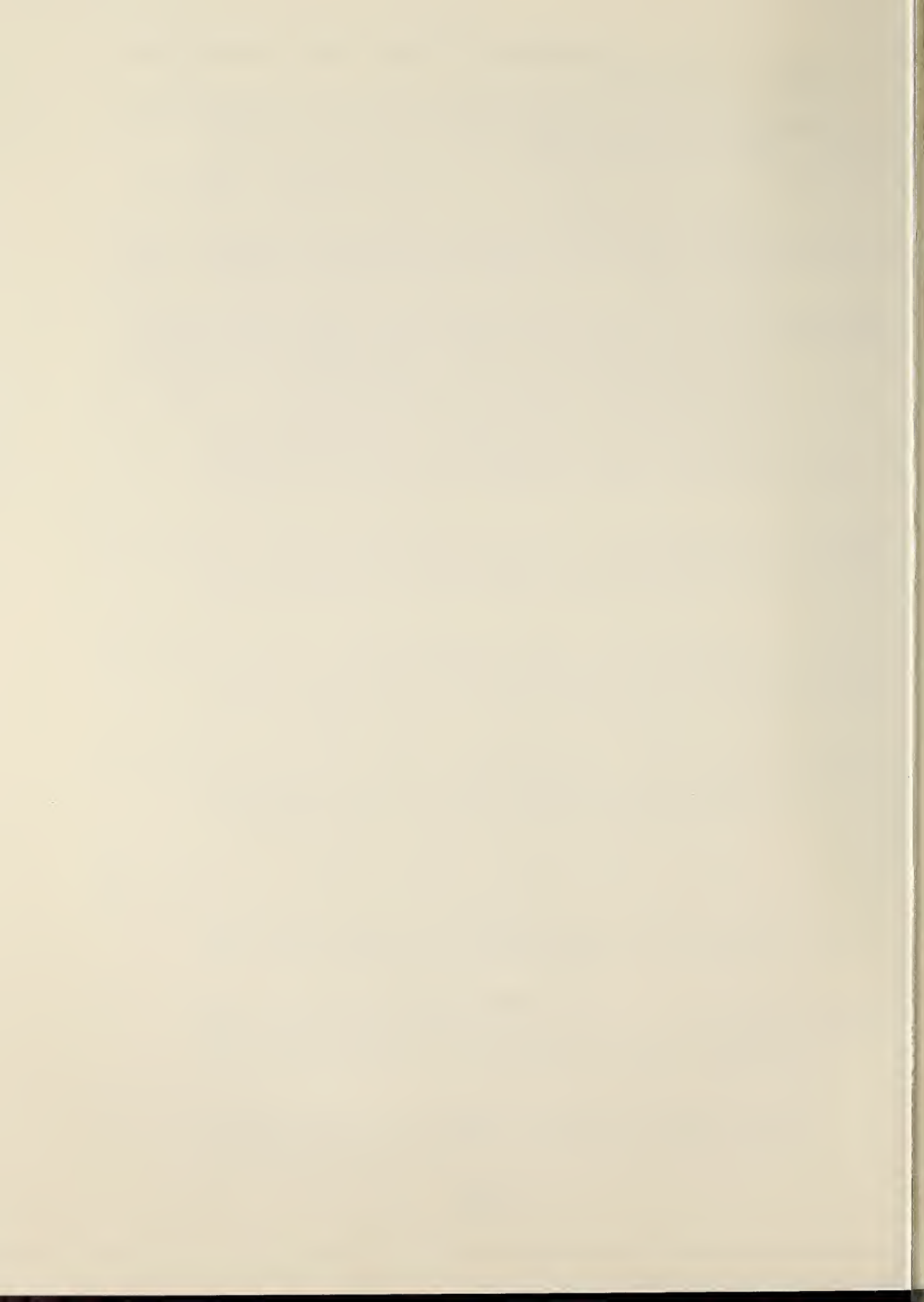
Mrs. Rosemary Maddock has continued to aid our group in the area of publications including the planning and preparation of illustrations and slides.

Miss Karen Loraski, our Section Secretary, has been with us almost a year. Her assistance in performing a variety of duties to the Section, including typing of complex manuscripts and reports, is greatly appreciated.

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- [4] Raspberry, S. D., Margoshes, M., and Scribner, B. F., "Applications of a Time-Sharing Computer in a Spectrochemistry Laboratory: Optical Emission and X-Ray Fluorescence," NBS Technical Note 407, Feb. 1968.
- [5] Veillon, C., and Margoshes, M., "A Pneumatic Solution Nebulization System Producing Dry Aerosol for Atomic Spectroscopy," Spectrochim. Acta, Part B, (in press).
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Certificate of Analysis

Standard Reference Materials 680 and 681

High-Purity and Doped Platinum¹

[NOTE: These materials are issued as interim standards to meet the needs of analysts working at trace level concentrations in platinum. The range of values reported represents the present state of the art in the cooperating laboratories.]

Element ²	SRM #680 High-Purity		SRM #681 Doped	
	Recommended Value	Range of Values Reported	Recommended Value	Range of Values Reported
Concentration in Parts per Million by Weight ³				
Copper	0.1	(0.087 — <1)	5.1 ^a	(2 — 6.3)
Silver	<0.1	(<0.06 — <1)	2.0 ^a	(1.4 — 2.1)
Palladium	0.2	(<0.1 — <1)	6 ^b	(4.0 — 6.1)
Lead	<1	(0.6 — 3)	12 ^c	(8.5 — 15)
Iron	0.7	(0.6 — 2.6)	5	(3.5 — 12)
Nickel	<1	(0.3 — <1)	0.5	(0.5 — <1)
Gold	<1	(<0.1 — 8)	9	(5 — 10)
Magnesium	<1	(<0.05 — 2)	12	(4.7 — 15)
Zirconium	<0.1	(<0.03 — 0.3)	11	(10.6 — 11.5)
Rhodium	<0.2	(0.09 — 0.1)	9	(5.2 — 10)
Iridium	<0.01	(0.007 — 0.01)	11	(5 — 18)
Oxygen	4	(3.2 — 5.2) *	7	(6.1 — 9.5) *

* Range from one laboratory only.

1. The platinum materials are in the form of wire 0.020 inch (0.51 mm) in diameter and are available in two lengths, 4 inches (10.2 cm) designated L-1 and 39.4 inches (1.0 m) designated L-2.

2. Other elements are also contained in the standards; some of them such as Al, Ca, Na, Si, and Sn may be certified at a later date.

3. The values listed are based on a consideration of the analytical methods and results reported by cooperating laboratories. Elements are listed in order of decreasing estimated accuracy for SRM 681. Close agreement among results from laboratories using different, reliable methods increases the degree of confidence in the recommended values, making possible estimates of accuracy for the following elements.

a. For Cu and Ag in SRM 681, values are estimated to be within 0.5 ppm of the actual value.

b. For Pd in SRM 681, values are estimated to be within 1 ppm of the actual value.

c. For Ph in SRM 681, values are estimated to be within 2 ppm of the actual value.

For other elements in SRM 681 and all elements in SRM 680, either because a single method was used or because of lack of agreement among methods, no estimate of accuracy can be made at this time. However, in about six months a revised certificate will be issued in which an attempt will be made to give estimate of accuracy.

Washington, D. C. 20234
December 28, 1967

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(over)

These standards have been established to provide homogeneous reference materials for the analysis of high-purity platinum, a material with extensive scientific and industrial applications, but a material the properties of which are greatly affected by the kind and amount of impurity elements. In cooperation with the National Bureau of Standards, the planning, preparation, homogeneity testing and analyses programs were conducted by the following organizations: Sigmund Cohn; Johnson, Matthey & Co., Ltd.; Engelhard Industries, Inc.; and RCA Laboratories.

The material for SRM No. 680 was prepared at Sigmund Cohn by induction melting of high-purity platinum sponge in a zirconium silicate crucible, and by casting into a platinum-lined, water-cooled copper mold. The ingot was trimmed, swaged, and drawn into wire using the utmost precautions to minimize contamination.

The material for SRM No. 681 was prepared at Engelhard Industries by induction melting under helium of high-purity platinum and a specially prepared pilot alloy containing the desired dopant elements. The melt was cast into a graphite mold and the ingot processed in a manner similar to SRM 680.

Extensive homogeneity testing was performed by NBS Washington and Boulder as well as by the four cooperating laboratories listed above using a combination of the following methods: optical emission and spark source mass spectrographic analyses; and electrical measurements including EMF, Temperature Coefficient of Resistivity (T.C.R.), and Residual Resistivity Ratio (RRR). Both lots of material were found to be homogeneous within the limits of precision of the analytical methods used at these trace levels. Elemental analyses were made at the National Bureau of Standards by one or more of the following methods: optical emission spectrography, spark source mass spectrography (isotopic dilution), polarography, spectrophotometry, activation analysis, and vacuum fusion.

Cooperating in this elemental analysis program were the following organizations who contributed emission spectrographic measurements:

J. Bishop & Co., Malvern, Pennsylvania

Engelhard Industries, Newark, New Jersey

Johnson, Matthey & Co., Ltd., London, England

CAUTION

Before use, it is recommended that possible surface contamination be removed by placing the sample in warm aqua regia ($3 \text{ HCl} + 1 \text{ HNO}_3$) for approximately five minutes, and then followed by rinsing in distilled water.

Certificate of Analysis

Standard Reference Material 1138, 1139

Cast Steel Standards

SRM No.	1138 Cast Steel 1	1139 Cast Steel 2
Element	Percent	
Carbon	0.12 ₀	0.79 ₂
Manganese	.43	.98
Phosphorus	.053	.01 ₁
Sulfur	.05 ₃	.013
Silicon	.34	.85
Copper	.09	.40
Nickel	.10	.9 ₃
Chromium	.12	1.96
Vanadium	.08	0.24
Molybdenum	.05	.51

SIZE AND METALLURGICAL CONDITION: Samples are approximately 1 1/4 inches square and 1/2 inch thick; they were chill-cast by a rapid unidirectional solidification technique.

CERTIFIED PORTION: The certified portion for each sample is that extending upward 5/16 inch from the chill-cast or test surface (the largest surface opposite the numbered surface). This portion only was analyzed in the cooperative program for certification.

PROVISIONAL CERTIFICATION: The provisional value listed for an element is the present best estimate of the true value based on the results of the cooperative analytical program. The provisional value is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for subscript figures, the deviation is not expected to be more than ± 5 in the subscript figure.

Washington, D. C. 20234
April 30, 1968

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(over)

PLANNING, PREPARATION, TESTING, ANALYSIS: The two cast steel standards are made available as a result of a cooperative program between the Steel Founders' Society of America and the National Bureau of Standards.

The material for the standards was melted and cast at the American Cast Iron Pipe Company, Birmingham, Ala. with use of the NBS chill-cast mold assembly. The preparation and homogeneity testing was similar to that described in NBS Misc. Publ. 260-1, Standard Reference Materials: Preparation of NBS White Cast Iron Spectrochemical Standards, Robert E. Michaelis and LeRoy L. Wyman, June 19, 1964.

Homogeneity testing was performed and found to be satisfactory for the elements certified. Chemical, optical emission, and x-ray analyses, or combinations thereof, were made at the National Bureau of Standards, the Research Laboratories of the General Motors Corporation, and the following member foundries of the Steel Founders' Society of America:

General Metals Corporation, Calif.
The Massillon Steel Castings Company, Ohio
Lebanon Steel Foundry, Pa.
The Duriron Company, Inc., Ohio
American Steel Foundries, Inc., Ind.
Esco Corporation, Oregon
Shenango-Penn, Ohio
Minneapolis Electric Steel Castings Company, Minn.
Ross-Meehan Foundries, Tenn.
Empire Steel Castings, Inc., Pa.

Chemical analyses for certification were made on representative samples for each standard at the National Bureau of Standards and the following member foundries of the American Steel Founders' Society of America:

Minneapolis Electric Steel Castings Company, Minn.
Esco Corporation, Oregon
Electric Steel Castings, Inc., Texas
Symington Wayne Corporation, New York
American Steel Foundries, Inc., Ind.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of B. F. Scribner.

The technical and support aspects involved in the preparation, certification, and issuance of these Standard Reference Materials were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

CAUTIONS:

1. Determinations made on other than the chill-cast or test surface are not recommended because of the unidirectional solidification structure.
2. These chill-cast standards are designed for calibration in the analysis of samples prepared in the same general manner; samples prepared by other casting techniques or having different metallurgical condition may exhibit a bias in the results.

Certificate of Analysis

Standard Reference Materials 1140, 1141, and 1142

Ductile Iron Standards

SRM No.	1140 Ductile Iron 1	1141 Ductile Iron 2	1142 Ductile Iron 3
Element	Percent		
Carbon	3.18	3.64	2.94
Manganese	0.72 ₅	0.48 ₀	0.18
Phosphorus	.007 ₀	.072	.20
Sulfur	.010	.020	.015
Silicon	1.92	1.11	3.33
Copper	0.10	0.21	1.0 ₂
Nickel	.028	.54	1.6 ₅
Chromium	.030	.14 ₅	0.05 ₃
Vanadium	.030	.009 ₀	.006
Molybdenum	.09 ₀	.05	.02 ₂
Titanium	.10	.013	.008
Aluminum	(.01) ^a	(.005)	(.09)
Arsenic	(.07)	(.04)	(.015)
Magnesium	.019	.04 ₄	.10
Cerium	(.09)	(.05)	(.015)
Yttrium	(<.002)	.04 ₀	.01

^a Values in parentheses are not certified but are provided for additional information on the composition.

SIZE AND METALLURGICAL CONDITION: Samples are approximately 1 1/4 inches square and 1/2 inch thick; they were chill-cast by a rapid unidirectional solidification technique.

CERTIFIED PORTION: The certified portion for each sample is that extending upward 5/16 inch from the chill-cast or test surface (the largest surface opposite the numbered surface). This portion only was analyzed in the cooperative program for certification.

PROVISIONAL CERTIFICATION: The provisional value listed for an element is the present best estimate of the true value based on the results of the cooperative analytical program. The provisional value is not expected to deviate from the true value by more than ± 1 in the last significant figure reported; for subscript figures, the deviation is not expected to be more than ± 5 in the subscript figure.

Washington, D. C. 20234
May 22, 1968

W. Wayne Meinke, Chief
Office of Standard Reference Materials

PLANNING, PREPARATION, TESTING, ANALYSIS: The three ductile iron standards are made available as a result of the cooperative program between the National Bureau of Standards and the American Cast Iron Pipe Company. The standards were developed at the request of the Ductile Iron Society and the American Foundrymen's Society.

The material for the standards was melted and cast at the American Cast Iron Pipe Company, Birmingham, Alabama, with use of the NBS chill-cast mold assembly. The preparation and homogeneity testing was similar to that described in NBS Misc. Publ. 260-1, Standard Reference Materials: Preparation of NBS White Cast Iron Spectrochemical Standards, Robert E. Michaelis and LeRoy L. Wyman, June 19, 1964.

Homogeneity testing was performed at NBS by D. M. Bouchette and was found to be satisfactory for the elements certified.

Analyses for certification were performed at NBS and included chemical (J. R. Baldwin), optical emission (D. M. Bouchette, J. L. Weber, Jr., M. M. Darr, and M. Margoshes), x-ray (S. D. Rasberry and M. M. Darr) and activation (P. D. LaFleur and G. J. Lutz). Analyses were performed at the American Cast Iron Pipe Company and included chemical (R. N. Smith and J. B. Hobby) and optical emission (I. Glaze and W. R. Kennedy).

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of B. F. Scribner.

The technical and support aspects involved in the preparation, certification, and issuance of these Standard Reference Materials were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

CAUTIONS:

1. Determinations made on other than the chill-cast or test surface are not recommended because of the unidirectional solidification structure.
2. These chill-cast standards are designed for calibration in the analysis of samples prepared in the same manner; samples prepared by other casting techniques or having other than a white structure may result in considerable bias.
3. Because the samples exhibit a change with respect to the columnar structure, both among standards and from bottom to top of the certified portion of the samples, the surface preparation for x-ray spectroscopic analysis may be critical. (A metallographic polishing technique is recommended).
4. Because of the poor heat conductivity of the ductile irons, difference in volatility rates for certain elements in emission spectroscopic analysis may occur depending on the location of the burn and the source parameters.

SUPPLEMENTAL INFORMATION

The elements boron, calcium, lead, and tin also are present in these standards. One or more may be certified at a later date.

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